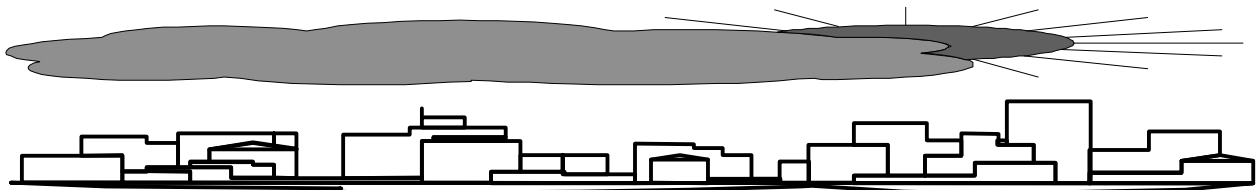




**EPA**

# **LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF LEAD AND LEAD COMPOUNDS**



# **L & E**

# Locating And Estimating Air Emissions From Sources of Lead and Lead Compounds

Office of Air Quality Planning and Standards  
Office of Air and Radiation  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

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This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and has been approved for publication. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

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## EXECUTIVE SUMMARY

The 1990 Clean Air Act Amendments contain a list of 188 hazardous air pollutants (HAPs) which the U.S. Environmental Protection Agency (EPA) must study, identify sources of, and determine if regulations are warranted.<sup>a</sup> Of these HAPs, lead and lead compounds are the subject of this document. This document describes the properties of lead and lead compounds as air pollutants, defines their production and use patterns, identifies source categories of air emissions, and provides lead emission factors. The document is a part of an ongoing EPA series designed to assist the general public at large, but primarily federal, state, and local air agencies, in identifying sources of HAPs and developing emissions estimates.

Lead is primarily used in the manufacture of lead-acid batteries, lead alloys, lead oxides in pigments, glass, lead cable coating, and a variety of lead products including ammunition and radiation shielding. Lead is emitted into the atmosphere from mining and smelting; from its use as a feedstock in the production of lead alloys, lead compounds and other lead-containing products; from mobile sources; and from combustion sources.

In addition to the lead and lead compound sources and emission factor data, information is provided that specifies how individual sources of lead and lead compounds may be tested to quantify air emissions.

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<sup>a</sup> Caprolactam was delisted from the list of HAPs (Federal Register Volume 61, page 30816, June 18, 1996).

SECTION 1.0  
PURPOSE OF DOCUMENT

The Environmental Protection Agency (EPA) and state and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate toxic emissions.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents that compiles available information on sources and emissions. Existing documents in the series are listed below.

<u>Substance or Source Category</u>	<u>EPA Publication Number</u>
Acrylonitrile	EPA-450/4-84-007a
Arsenic	EPA-454/R-98-011
Benzene	EPA-450/4-84-007q
1,3-Butadiene	EPA-454/R-96-008
Cadmium	EPA-454/R-93-040
Carbon Tetrachloride	EPA-450/4-84-007b
Chlorobenzenes (revised)	EPA-454/R-93-044
Chloroform	EPA-450/4-84-007c
Chromium	EPA-450/4-84-007g
Chromium (supplement)	EPA-450/2-89-002

<u>Substance or Source Category</u>	<u>EPA Publication Number</u>
Coal and Oil Combustion Sources	EPA-450/2-89-001
Cyanide Compounds	EPA-454/R-93-041
Dioxins and Furans	EPA-454/R-97-003
Epichlorohydrin	EPA-450/4-84-007j
Ethylene Oxide	EPA-450/4-84-007l
Ethylene Dichloride	EPA-450/4-84-007d
Formaldehyde	EPA-450/2-91-012
Lead	EPA-454/R-98-006
Manganese	EPA-450/4-84-007h
Medical Waste Incinerators	EPA-454/R-93-053
Mercury and Mercury Compounds	EPA-453/R-93-023
Methyl Chloroform	EPA-454/R-93-045
Methyl Ethyl Ketone	EPA-454/R-93-046
Methylene Chloride	EPA-454/R-93-006
Municipal Waste Combustors	EPA-450/2-89-006
Nickel	EPA-450/4-84-007f
Organic Liquid Storage Tanks	EPA-450/4-88-004
Perchloroethylene and Trichloroethylene	EPA-450/2-90-013
Phosgene	EPA-450/4-84-007i
Polychlorinated Biphenyls (PCB)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM)	EPA-450/4-84-007p
Sewage Sludge Incineration	EPA-450/2-90-009
Styrene	EPA-454/R-93-011
Toluene	EPA-454/R-93-047
Vinylidene Chloride	EPA-450/4-84-007k
Xylenes	EPA-454/R-93-048

This document deals specifically with lead and lead compounds. Its intended audience includes federal, state and local air pollution personnel and others who are interested in locating potential emitters of lead and lead compounds and making gross emissions estimates.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. This document is intended to be used as a tool to assist in inventorying lead air emissions from source categories, rather than specific facilities. Available data are insufficient to develop statistical estimates of the accuracy of these emission factors, so no estimate can be made of the error that could result when these factors are used to calculate emissions from any given facility. The public's misinterpretation of these figures can lead to a gross exaggeration of lead air emissions. It is possible, in some cases, that order-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices.<sup>1</sup> Thus, in situations where an accurate assessment of lead emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test should be considered as the best means to determine air emissions directly from a facility or operation.

A national ambient air quality standard (NAAQS) for lead of 1.5 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) averaged over a calendar quarter was established in 1978. The EPA used health effects criteria as the basis for arriving at this level for the NAAQS. As such, a large amount of health-related information does exist in available literature for lead.

Since establishing the NAAQS for lead in 1978, EPA has periodically reviewed the standard, again focusing on the health effects of lead. Although the NAAQS limit has remained unchanged at  $1.5 \mu\text{g}/\text{m}^3$ , evaluation of the standard is ongoing at EPA, generating additional health-related and ambient air concentration data. However, data collected through ambient air studies do not reveal specific lead emission contributions from individual sources, which is the focus of this document.

With the 1990 Amendments to the CAA, lead and lead compounds were both recognized for their toxic characteristics and included on the list of hazardous air pollutants



(HAPs) presented in Section 112(d) to be evaluated in the development of maximum achievable control technology (MACT) standards. In addition, many states also recognize lead and lead compounds as toxic pollutants, and some states may impose their own regulations, which can be more stringent than federal standards. For example, under the state of California's air toxic identification and control program, the California Air Resources Board (CARB) is proposing to identify inorganic lead as a toxic air contaminant. The identification or risk assessment process includes assessing the exposure and health effects of toxic air contaminants. Once a toxic air contaminant is identified by the Board, it enters into the control or risk management phase of the program. In this phase, the need for an appropriate degree of controls is evaluated with full public participation.<sup>2</sup>

Lead air emissions have also been affected by regulatory activity from other agencies, including: the Occupational Safety and Health Administration (OSHA), which has enacted regulations for reducing lead exposure to a variety of worker categories; the U.S. Consumer Product Safety Commission, which has prohibited lead paints on toys and furniture; the Food and Drug Administration (FDA) has guidelines for levels of lead that can leach out of ceramics; and the Toxic Substances Control Act (TSCA) which proposed reducing lead in the manufacture of certain products, such as fishing sinkers.

The MACT standards development program at the Office of Air Quality Planning and Standards (OAQPS) has served as a means of providing source-specific information on lead and lead compound emissions. A concerted effort was made during the development of this document to coordinate with the work underway at OAQPS. Data were available through this program for the metallurgical industry, which is a significant emitter of lead. However, many of the MACT standards were in the preliminary stages (e.g., secondary aluminum, iron and steel foundries), and emissions information was not available.

As a result of California's "Hot Spots" source testing program and other state source testing efforts, data were available for incorporation into this document. Information and

test data from these reports are maintained in EPA's Source Test Information Retrieval System (STIRS) database and the Factor Information Retrieval (FIRE) System.<sup>3,4</sup> However, despite the data generated by these programs, the available data on some potential sources of lead emissions are limited and the configurations of many sources will not be the same as those described in this document. Therefore, this document is best used as a primer to inform air pollution personnel about the following: (1) the types of sources that may emit lead, (2) process variations that may be expected within these sources affecting emissions, and (3) available emissions information that indicates the potential for lead to be released into the air from each operation. This document does not contain any discussion of health or other environmental effects of lead, nor does it include any discussion of ambient air levels.

As standard procedure, L&E documents are sent to government, industry, and environmental groups wherever EPA is aware of expertise. These groups are given the opportunity to review a document, comment, and provide additional data, where applicable. Although this document has undergone extensive review, there may still be shortcomings. Comments subsequent to publication are welcome and will be addressed based on available time and resources. In addition, any comments on the contents or usefulness of this document are welcome, as is any information on process descriptions, operating practices, control measures, and emissions information that would enable EPA to update and improve the document's contents. All comments should be sent to:

Group Leader  
Emission Factor and Inventory Group (MD-14)  
Office of Air Quality Planning and Standards  
U. S. Environmental Protection Agency  
Research Triangle Park, North Carolina 27711

## SECTION 2.0

### OVERVIEW OF DOCUMENT CONTENTS

This section briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3.0 provides a brief summary of the physical and chemical characteristics of lead and lead compounds and an overview of its production, uses, and emission sources. This background section is useful in developing a general perspective on lead, how it is manufactured and consumed, and identifies potential sources of lead emissions.

Section 4.0 focuses on air emissions of lead from the metallurgical industry. For each major production source category described in Section 4.0, a list of individual companies identified in that particular industry is provided, where available. An example process description and a flow diagram with potential lead emission points are given. Emission factors for potential lead emissions, before and after controls employed by industry, are given where available.

Section 5.0 describes various combustion source categories where lead emissions have been reported. For each type of combustion source, a description(s) of the combustor is given and potential lead emission points are identified on diagrams. Emission factors for potential lead emissions, before and after controls, are given where available.

Section 6.0 summarizes other source categories that use and potentially emit lead. The manufacture of lead-acid batteries is discussed in this section. The majority of the other source categories discussed use lead as an additive in various products such as glass, paint,

pigments, glazes, solders, and stabilizers. Limited information on many of these sources is available; therefore, varying levels of detail on the processes, emissions, and controls are presented. Locations of facilities in each source category are provided, where available.

Section 7.0 discusses lead emissions from mobile sources. Both on-road and off-road sources, as well as aircraft are addressed. This section also includes a discussion of emissions from lead deposited in soil by mobile sources and reentrained in road dust.

Section 8.0 summarizes available procedures for source sampling, ambient air monitoring, and analysis of lead. This section provides an overview of applicable sampling procedures and cites references for those interested in conducting source tests. References for the entire document are listed in Section 9.0.

Appendix A presents a summary table of the emission factors contained in this document. This table also presents the factor quality rating and the Source Classification Code (SCC) or Area/Mobile Source (AMS) code associated with each emission factor.

Each emission factor listed in Sections 4.0 through 7.0 was assigned an emission factor rating (A, B, C, D, E, or U) based on the criteria for assigning data quality ratings and emission factor ratings as required in the document *Procedures for Preparing Emission Factor Documents*.<sup>5</sup> The criteria for assigning the data quality ratings to source tests are as follows:

- A - Tests are performed by using an EPA reference test method, or when not applicable, a sound methodology. Tests are reported in enough detail for adequate validation, and, raw data are provided that can be used to duplicate the emission results presented in the report.
- B - Tests are performed by a generally sound methodology, but lacking enough detail for adequate validation. Data are insufficient to completely duplicate the emission result presented in the report.
- C - Tests are based on an unproven or new methodology, or are lacking a significant amount of background information.

- D - Tests are based on generally unacceptable method, but the method may provide an order-of-magnitude value for the source.

Once the data quality ratings for the source tests had been assigned, these ratings along with the number of source tests available for a given emission point were evaluated. Because of the almost impossible task of assigning a meaningful confidence limit to industry-specific variables (e.g., sample size vs. sample population, industry and facility variability, method of measurement), the use of a statistical confidence interval for establishing a representative emission factor for each source category was not practical. Therefore, some subjective quality rating was necessary. The following quality ratings were used in the emission factor tables in this document:

- A - Excellent. Emission factor is developed primarily from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category population is sufficiently specific to minimize variability.
- B - Above average. Emission factor is developed primarily from A- or B-rated test data from a moderate number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.
- C - Average. Emission factor is developed primarily from A-, B-, and C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.
- D - Below average. Emission factor is developed primarily from A-, B-, and C-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population.
- E - Poor. Factor is developed from C- rated and D-rated test data from a very few number of facilities, and there may be reasons to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

- U - Unrated (Only used in the L&E documents). Emission factor is developed from source tests which have not been thoroughly evaluated, research papers, modeling data, or other sources that may lack supporting documentation. The data are not necessarily “poor,” but there is not enough information to rate the factors according to the rating protocol.

## SECTION 3.0 BACKGROUND

### 3.1 PHYSICAL AND CHEMICAL NATURE OF LEAD AND LEAD COMPOUNDS

Pure lead is a silvery-white metal that oxidizes and turns bluish-gray when exposed to air. It is soft enough to be scratched with a fingernail. It is dense, malleable, and readily fusible.<sup>6</sup> Its properties include a low melting point; ease of casting; high density; low strength; ease of fabrication; acid resistance; electrochemical reaction with sulfuric acid; chemical stability in air, water, and earth; and the ability to attenuate sound waves, atomic radiation and mechanical vibration.<sup>7</sup> The physical properties of lead are presented in Table 3-1.

Lead in its elemental or pure form rarely occurs in nature. Lead most commonly occurs as the mineral galena (lead sulfide [PbS]), and is sometimes found in other mineral forms, which are of lesser commercial importance, such as anglesite (PbSO<sub>4</sub>) and cerussite (PbCO<sub>3</sub>).<sup>6</sup> Table 3-2 presents properties of these three mineral compounds.

Lead is hardened by alloying it with small amounts of arsenic, copper, antimony, or other metals.<sup>6</sup> These alloys are frequently used in manufacturing various lead-containing products. A list of typical end uses for lead alloys is given in Table 3-3.

TABLE 3-1. PHYSICAL PROPERTIES OF LEAD

Property	Value
Atomic weight	207.2g
Melting point	327°C
Boiling point	1770°C
Specific gravity	
20°C	11.35 g/cm <sup>3</sup>
327°C (solid)	11.00 g/cm <sup>3</sup>
327°C (liquid)	10.67 g/cm <sup>3</sup>
Specific heat	130 J/(kg-K) <sup>a</sup>
Latent heat of fusion	25 J/g <sup>a</sup>
Latent heat of vaporization	860 J/g <sup>a</sup>
Vapor pressure	
980°C	0.133 kPa <sup>b</sup>
1160°C	1.33 kPa <sup>b</sup>
1420°C	13.33 kPa <sup>b</sup>
1500°C	26.7 kPa <sup>b</sup>
1600°C	53.3 kPa <sup>b</sup>
Thermal conductivity	
28°C	34.7 W/(m-K)
100°C	33.0 W/(m-K)
327°C (solid)	30.5 W/(m-K)
327°C (liquid)	24.6 W/(m-K)
Thermal conductivity (relative to Ag = 100)	8.2
Coefficient of linear expansion, at 20°C per °C	29.1x10 <sup>-6</sup>
Surface tension at 360°C, mN/m (= dyn/cm)	442

Source: Reference 8

<sup>a</sup> To convert J to cal, divide by 4.184.<sup>b</sup> To convert kPa to mm Hg, multiply by 7.5.



TABLE 3-2. PHYSICAL PROPERTIES OF THE PRINCIPAL LEAD-ORE COMPOUNDS

	Galena	Cerussite	Anglesite
Formula	PbS	PbCO <sub>3</sub>	PbSO <sub>4</sub>
Lead, percent	86.6	77.5	68.3
Hardness, Mohs scale	2.5 to 2.75	3 to 3.5	2.5 to 3
Luster	Metallic	Adamantine to vitreous, resinous	Adamantine to vitreous, resinous
Color	Lead gray	Colorless to white	Colorless to white
Density, g/cm <sup>3</sup>	7.58	6.55	6.38

Source: Reference 9

Lead in its compound form also has many uses in manufacturing processes, primarily as pigments. Lead compounds can be classified into the following general categories:

- Organolead compounds;
- Lead oxides;
- Lead sulfides; and
- Lead salts.

Each of these classes of lead compounds is discussed briefly below. Table 3-4 presents a summary of the chemical formulas and end uses of the most commonly used lead compounds.

#### 3.1.1 Organolead Compounds

Organolead compounds are distinctive with at least one lead-carbon bond. Only two types of organolead compounds have found large-scale commercial applications: tetramethyllead (TML) and tetraethyllead (TEL). However, with the removal of lead from

TABLE 3-3. USES OF LEAD ALLOYS

Alloy	Uses
Lead - Copper	
<0.10% copper by wt.	<ul style="list-style-type: none"> <li>Lead sheet</li> <li>Lead pipes</li> <li>Sheathings for electric power cables</li> <li>Wire and other fabricated lead products</li> <li>Tank linings</li> <li>Tubes for acid-mist precipitators</li> <li>Steam heating pipes for acid-plating baths</li> </ul>
60 to 70% copper by wt. (leaded brass or bronze)	<ul style="list-style-type: none"> <li>Bearings and bushings</li> </ul>
Lead - Antimony	<ul style="list-style-type: none"> <li>Lead-acid battery positive grids, posts, and connectors</li> <li>Flashings and roofing materials</li> <li>Cable sheathings</li> <li>Ammunition</li> <li>Tank linings, pumps, valves, pipes, and heating and cooling coils in chemical operations using sulfuric acid or sulfate solutions at elevated temperatures</li> <li>Lead sheet</li> <li>Anodes in metal-plating and metal-electrowinning operations</li> <li>Collapsible tubes</li> <li>Wheel-balancing weights for automobiles and trucks</li> <li>Special weights and castings</li> <li>Battery cable clamps</li> </ul>
Lead - Antimony - Tin	<ul style="list-style-type: none"> <li>Printing-type metals</li> <li>Bushing and sleeve bearings</li> <li>Journal bearings in freight cars and mobile cranes</li> <li>Decorative, slush, and special castings (e.g., miniature figures, casket trim, belt buckles, trophies, and holloware)</li> </ul>
Lead - Tin	<ul style="list-style-type: none"> <li>Solders for sealing and joining metals (e.g., electronic applications including printed circuit boards)</li> <li>Automobile radiators</li> <li>High-temperature heat exchangers</li> <li>Terne-steel sheets for radio and television chassis, roofs, fuel tanks, air filters, oil filters, gaskets, metal furniture, gutters, and downspouts</li> <li>Coating of copper sheet used for building flashings</li> <li>Coating of steel and copper electronic components</li> <li>Electroplating</li> </ul>
Lead - Calcium	<ul style="list-style-type: none"> <li>Grids for large stationary stand-by power, submarine, and specialty sealed batteries</li> <li>Original equipment automotive batteries</li> <li>Negative grids for replacement batteries</li> <li>Electrowinning anodes</li> <li>Cable sheathing, sleeving for cable splices, specialty boat keels, and lead-alloy tapes</li> </ul>
Lead - Calcium - Aluminum	<ul style="list-style-type: none"> <li>Negative battery grids</li> </ul>

TABLE 3-3. USES OF LEAD ALLOYS (CONTINUED)

Alloy	Uses
Lead - Calcium - Tin	Maintenance-free automotive battery grids Electrowinning anodes
Lead - Silver	Insoluble anodes for zinc and manganese electroplating Anodes in the d-c cathodic protection of steel pipe and structures used in fresh, brackish, or seawater Solder in high pressure, high temperature cooling systems Positive grids of lead-acid batteries Soft solders
Lead - Silver - Antimony	Production of thin copper foil for electronics
Lead - Silver - Calcium	Zinc electrowinning
Lead - Strontium - Tin	Maintenance-free battery grids Bearings
Lead - Tellurium	Used in pipes and sheets for chemical installations Shielding for nuclear reactors Cable sheathing
Fusible (lead, cadmium, bismuth, and tin in varying compositions) <sup>a</sup>	Fuses Low-melting sprinkler systems Foundry patterns Molds, dies, punches, chucks, cores, mandrels, flexible tubing, and low-temperature solder
Lead - Iridium	Used to solder metals to glass
Lead - Lithium and Lead - Lithium - Tin	Battery grids Bearings

Source: Reference 10

<sup>a</sup> Alloys that melt at very low temperatures (i.e., 32°F to 361.4°F [0°C to 183°C]).

TABLE 3-4. LEAD COMPOUNDS

Compound	Chemical Formula or Description	Uses
Lead acetate	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	Dyeing of textiles, waterproofing, varnishes, lead driers, chrome pigments, gold cyanidation process, insecticide, anti-fouling paints, analytical reagent, hair dye
Lead alkyl, mixed	A mixture containing various methyl and ethyl derivatives of tetraethyl lead and tetramethyl lead	Anti-knock agents in aviation gasoline
Lead antimonate	$\text{Pb}_3(\text{SbO}_4)_2$	Staining glass, crockery, and porcelain
Lead arsenate	$\text{Pb}_3(\text{AsO}_4)_2$	Insecticide, herbicide
Lead arsenite	$\text{Pb}(\text{AsO}_2)_2$	Insecticide
Lead azide	$\text{Pb}(\text{N}_3)_2$	Primary detonating compound for high explosives
Lead borate	$\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$	Varnish and paint drier, waterproofing paints, lead glass, electrically conductive ceramic coatings
Lead borosilicate	Composed of a mixture of the borate and silicate of lead	A constituent of optical glass
Lead carbonate, basic	$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	Exterior paint pigments, ceramic glazes
Lead chloride	$\text{PbCl}_2$	Preparation of lead salts, lead chromate pigments, analytical reagent
Lead chromate	$\text{PbCrO}_4$	Pigment in industrial paints, rubber, plastics, ceramic coatings; organic analysis
Lead cyanide	$\text{Pb}(\text{CN})_2$	Metallurgy
Lead dimethyldithiocarbamate	$\text{Pb}[\text{SCSN}(\text{CH}_3)_2]_2$	Vulcanization accelerator with litharge
Lead dioxide	$\text{PbO}_2$	Oxidizing agent, electrodes, lead-acid storage batteries, curing agent for polysulfide elastomers, textiles (mordant, discharge in dyeing with indigo), matches, explosives, analytical reagent.
Lead fluoborate	$\text{B}_2\text{F}_8 \cdot \text{Pb}$	Salt for electroplating lead; can be mixed with stannous fluoborate to electroplate any composition of tin and lead as an alloy

TABLE 3-4. LEAD COMPOUNDS (CONTINUED)

Compound	Chemical Formula or Description	Uses
Lead fluoride	$\text{PbF}_2$	Electronic and optical applications, starting materials for growing single-crystal solid-state lasers, high-temperature dry film lubricants in the form of ceramic-bonded coatings
Lead fluosilicate	$\text{PbSiF}_6 \cdot 2\text{H}_2\text{O}$	Solution for electrorefining lead
Lead formate	$\text{Pb}(\text{CHO}_2)_2$	Reagent in analytical determinations
Lead hydroxide	$\text{Pb}(\text{OH})_2$	Lead salts, lead dioxide
Lead iodide	$\text{PbI}_2$	Bronzing, printing, photography, cloud seeding
Lead linoleate	$\text{Pb}(\text{C}_{18}\text{H}_{31}\text{O}_2)_2$	Medicine, drier in paints and varnishes
Lead maleate, tribasic	$\text{C}_4\text{H}_6\text{O}_5 \cdot \text{Pb}$	Vulcanizing agent for chlorosulfonated polyethylene. Highly basic stabilizer with high heat stability in vinyls
Lead molybdate	$\text{PbMoO}_4$	Analytical chemistry, pigments
Lead $\beta$ -naphthalenesulfonate	$\text{Pb}(\text{C}_{10}\text{H}_7\text{SO}_3)_2$	Organic preparations
Lead naphthenate	$\text{C}_7\text{H}_{12}\text{O}_2 \cdot x\text{Pb}$	Paint and varnish drier, wood preservative, insecticide, catalyst for reaction between unsaturated fatty acids and sulfates in the presence of air, lube oil additive
Lead nitrate	$\text{Pb}(\text{NO}_3)_2$	Lead salts, mordant in dyeing and printing calico, matches, mordant for staining mother of pearl, oxidizer in the dye industry, sensitizer in photography, explosives, tanning, process engraving, and lithography
Lead oleate	$[\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COO}]_2\text{Pb}$	Varnishes, lacquers, paint drier, high-pressure lubricants
Lead oxide, red	$\text{Pb}_3\text{O}_4$	Storage batteries, glass, pottery, and enameling, varnish, purification of alcohol, packing pipe joints, metal-protective paints, fluxes and ceramic glazes.
Lead phosphate	$\text{Pb}_3(\text{PO}_4)_2$	Stabilizing agent in plastics
Lead phosphate, dibasic	$\text{PbHPO}_4$	Imparting heat resistance and pearlescence to polystyrene and casein plastics

TABLE 3-4. LEAD COMPOUNDS (CONTINUED)

Compound	Chemical Formula or Description	Uses
Lead phosphite, dibasic	$2\text{PbO} \cdot \text{PbHPO}_3 \cdot 1/2\text{H}_2\text{O}$	Heat and light stabilizer for vinyl plastics and chlorinated paraffins. As a UV screening and antioxidizing stabilizer for vinyl and other chlorinated resins in paints and plastics
Lead phthalate, dibasic	$\text{C}_6\text{H}_4(\text{COO})_2\text{Pb} \cdot \text{PbO}$	Heat and light stabilizer for general vinyl use
Lead resinate	$\text{Pb}(\text{C}_{20}\text{H}_{29}\text{O}_2)_2$	Paint and varnish drier, textile waterproofing agent
Lead salicylate	$\text{Pb}(\text{OOC}_6\text{H}_4\text{OH})_2 \cdot \text{H}_2\text{O}$	Stabilizer or costabilizer for flooring and other vinyl compounds requiring good light stability
Lead sesquioxide	$\text{Pb}_2\text{O}_3$	Ceramics, ceramic cements, metallurgy, varnishes
Lead silicate	$\text{PbSiO}_3$	Ceramics, fireproofing fabrics
Lead silicate, basic	A pigment made up of an adherent surface layer of basic lead silicate and basic lead sulfate cemented to silica	Pigment in industrial paints
Lead silicochromate	A yellow lead-silicon pigment	Normal lead silicon chromate is used as a yellow prime pigment for traffic marking paints. Basic lead silicon chromate is used as a corrosive inhibitive pigment for metal protective coatings, primers, and finishers. Also for industrial enamels requiring a high gloss
Lead sodium thiosulfate	$\text{PbS}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3$	Matches
Lead stannate	$\text{PbSnO}_3 \cdot 2\text{H}_2\text{O}$	Additive in ceramic capacitors, pyrotechnics
Lead stearate	$\text{Pb}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	Varnish and lacquer drier, high-pressure lubricants, lubricant in extrusion processes stabilizer for vinyl polymers, corrosion inhibitor for petroleum, component of greases, waxes, and paints
Lead subacetate	$2\text{Pb}(\text{OH})_2\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	Decolorizing agent (sugar solutions, etc.)
Lead suboxide	$\text{Pb}_2\text{O}$	In storage batteries
Lead sulfate	$\text{PbSO}_4$	Storage batteries, paint pigments
Lead sulfate, basic	$\text{PbSO}_4 \cdot \text{PbO}$	Paints, ceramics, pigments

TABLE 3-4. LEAD COMPOUNDS (CONTINUED)

Compound	Chemical Formula or Description	Uses
Lead sulfate, blue basic	Composition: Lead sulfate (min) 45%, lead oxide (min) 30%, lead sulfide (max) 12%, lead sulfite (max) 5%, zinc oxide 5%, carbon and undetermined matter (max) 5%	Components of structural-metal priming coat paints, rust-inhibitor in paints, lubricants, vinyl plastics, and rubber products
Lead sulfate, tribasic	$3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$	Electrical and other vinyl compounds requiring high heat stability
Lead sulfide	$\text{PbS}$	Ceramics, infrared radiation detector, semi-conductor, ceramic glaze, source of lead
Lead telluride	$\text{PbTe}$	Single crystals used as photoconductor and semiconductor in thermocouples
Lead tetraacetate	$\text{Pb}(\text{CH}_3\text{COO})_4$	Oxidizing agent in organic synthesis, laboratory reagent
Lead thiocyanate	$\text{Pb}(\text{SCN})_2$	Ingredient of priming mix for small-arms cartridges, safety matches, dyeing
Lead titanate	$\text{PbTiO}_3$	Industrial paint pigment
Lead tungstate	$\text{PbWO}_4$	Pigment
Lead vanadate	$\text{Pv}(\text{VO}_3)_2$	Preparation of other vanadium compounds, pigment
Lead zirconate titanate	$\text{PbTiZrO}_3$	Element in hi-fi sets and as a transducer for ultrasonic cleaners, ferroelectric materials in computer memory units
Litharge	$\text{PbO}$	Storage batteries, ceramic cements and fluxes, pottery and glazes, glass, chromium pigments, oil refining, varnishes, paints, enamels, assay of precious metal ores, manufacture of red lead, cement (with glycerol), acid-resisting compositions, match-head compositions, other lead compounds, rubber accelerator

Source: Reference 11

gasoline, these compounds are no longer produced in the United States, although they are imported for special applications such as use in aircraft fuel.

### 3.1.2 Lead Oxides

Lead oxide is a general term and includes lead monoxide or “litharge” ( $\text{PbO}$ ); lead tetraoxide or “red lead” ( $\text{Pb}_3\text{O}_4$ ); and black or “gray” oxide, which is a mixture of 70 percent lead monoxide and 30 percent metallic lead. Litharge is used primarily in the manufacture of various ceramic products. Because of its electrical and electronic properties, litharge is also used in capacitors and electrophotographic plates, as well as in ferromagnetic and ferroelectric materials. It is also used as an activator in rubber, a curing agent in elastomers, a sulfur removal agent in the production of thiols and in oil refining, and an oxidation catalyst in several organic chemical processes. It also has important markets in the production of many lead chemicals, dry colors, soaps (i.e., lead stearate), and driers for paint. Another important use of litharge is the production of lead salts, particularly those used as stabilizers for plastics, notably polyvinyl chloride materials.<sup>12</sup>

Lead tetraoxide or red lead is a brilliant orange-red pigment. It is used as a pigment in anticorrosion paints for steel surfaces. It is also used in lead oxide pastes for tubular storage batteries, in ballistic modifiers for high-energy propellants, in ceramic glazes for porcelain, in lubricants for hot pressing metals, in radiation-shielding foam coatings in clinical x-ray exposure, and in rubber adhesives for roadway joints.<sup>10</sup> Black lead is made for specific use in the manufacture of lead acid storage batteries.<sup>12</sup>

Lead dioxide ( $\text{PbO}_2$ ) is a brownish, black powder. Because of its strong oxidizing properties, it is used in the manufacture of dyes and to control burning in incendiary fires. It is also used as a curing agent for liquid polysulfide polymers and low molecular weight butyl and polyisopropane.<sup>13</sup>



Lead titanate ( $\text{PbTiO}_3$ ) and lead zirconate ( $\text{PbZrO}_3$ ) are two lead oxides that are frequently mixed, resulting in highly desirable piezoelectric properties that are used in high-power acoustic radiating transducers, hydrophones, and specialty instruments.<sup>14</sup>

### 3.1.3 Lead Sulfides

Lead sulfide ( $\text{PbS}$ ) or galena is one of the most common lead minerals, appearing black and opaque. It is an efficient heat conductor and has semiconductor properties, making it desirable for use in photoelectric cells. Lead sulfide is used in ceramics, infrared radiation detectors, and ceramic glaze.<sup>14,15</sup>

### 3.1.4 Lead Salts

Most lead salts are white or colorless and are used commercially as pigments. Basic lead carbonate ( $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ ), basic lead sulfate ( $\text{Pb}(\text{SO}_4) \cdot \text{PbO}$ ), and basic lead silicates ( $3\text{PbO} \cdot \text{SiO}_2$ ) are well known white pigments. Basic lead carbonate is used as a component of ceramic glazes, as a curing agent with peroxides to form improved polyethylene wire insulation, as a color-changing component of temperature-sensitive inks, as a component of lubricating greases, and as a component of weighted nylon-reinforced fish nets made of polyvinylchloride (PVC) fibers.<sup>10</sup>

Basic lead sulfate helps provide efficient, long-term, economic heat stability to flexible and rigid PVC. It can be dispersed easily, and has excellent electrical insulation properties. It is also an effective activator for azodicarbonamide blowing agents for vinyl foams.<sup>10</sup>

Basic lead silicates are used by the glass, ceramic, paint, rubber, and plastics industries. Lead monosilicate ( $3\text{PbO} \cdot 3\text{SiO}_2$ ) is used in formulating lead-bearing glazes for the ceramics industry and as a source of  $\text{PbO}$  in the glass industry. Lead bisilicate ( $\text{PbO} \cdot \text{O}_3\text{Al}_2\text{O}_3 \cdot 1.95\text{SiO}_2$ ) was developed as a low solubility source of lead in ceramic glazes for foodware. Tribasic lead silicate ( $3\text{PbO} \cdot \text{SiO}_2$ ) is used primarily by glass and frit producers.<sup>10</sup>

Lead chromates ( $\text{PbCrO}_4$ ), colored salts, are used frequently as orange and yellow pigments.<sup>11</sup>

Lead borates [ $\text{Pb}(\text{BO}_2)_2\text{H}_2\text{O}$ ], germanates ( $\text{PbO}\cdot\text{GeO}_2$ ), and silicates ( $\text{PbO}\cdot\text{SiO}_2$ ) are glass-forming compounds that impart unique properties to glasses, enamels, glazes, and other ceramics. Other salts are used as stabilizers for plastics and rubbers, explosives, and in electroplating.<sup>10,11</sup>

### 3.2 OVERVIEW OF PRODUCTION AND USE

Lead is produced in one of two ways: either by primary production through mining of ores or secondary production through recycling. According to the U.S. Bureau of Mines, the 1992 domestic production of recoverable lead from lead ores was 437,715 tons (397,923 Mg), or 22 percent of the total lead produced domestically. The 1992 domestic refined lead recovered from lead scrap was 1,008,257 tons (916,597 Mg), or 78 percent of the total lead produced domestically.<sup>16</sup>

In 1992, domestic lead ore mining in the United States accounted for about 13 percent of the total world lead mine production for that year. Australia, Canada, China, and Kazakhstan (formerly part of the U.S.S.R.) accounted for nearly 47 percent of the world's lead mine production in 1992. Other major lead ore producing countries include Mexico, North Korea, Morocco, Peru, South Africa, Sweden, and other nations part of the former U.S.S.R.<sup>16</sup>

Most of the lead ore mined in the United States comes from the “lead-belt” in southeast Missouri. The recoverable lead mine production from Missouri was about 76 percent of the total lead mine production in the United States in 1992. In Missouri, lead is primarily recovered from lead, zinc, and lead-zinc ores. Lead is also mined in Alaska, Arizona, Colorado, Idaho, Illinois, Montana, New Mexico, New York, and Tennessee. In these states, lead is recovered from zinc, lead-zinc, copper, gold, and fluor spar ore deposits.<sup>16</sup>

Lead ore is mined underground except when it is mined with copper ores, which are typically mined in open pits. The lead content of ores typically ranges from 3 to 8 percent. The ores are processed at the mine site to produce a lead ore concentrate of 55 to 70 percent lead. Once dried, the lead-ore concentrates are shipped to primary lead smelter/refinery plants for further processing.

Lead ore concentrates are processed at primary lead smelter/refinery plants to produce lead metal or alloys. In 1992, primary lead smelter/refinery plants operating in the United States produced 335,270 tons (304,791 Mg) of refined lead.<sup>16</sup> These smelters/refineries were the following: ASARCO (with smelter located in East Helena, MT, and refinery located in Omaha, NE); ASARCO (with both smelter and refinery located in Glover, MO); and Doe Run (with both smelter and refinery located in Herculaneum, MO).

Lead is among the most recycled nonferrous metals in the world. Secondary production (from recycled materials) has risen steadily, such that in 1992, secondary output surpassed primary output in the United States by about a factor of three. This growth reflects the favorable economic conditions associated with lead recycling and the ability of lead to retain its physical and chemical properties when recycled.<sup>17</sup>

Secondary lead smelters and refineries recover and refine metal from lead-bearing scrap materials and residues to produce lead and lead alloy ingots, lead oxide, and lead pigments. About 86 percent of recycled scrap was from lead-acid battery plates.<sup>16</sup>

In 1992, 1,330,228 tons (1,236,571 Mg) of lead were consumed by product manufacturing sectors in the United States. Figure 3-1 shows the various manufacturing sectors consuming lead in 1992.<sup>16</sup>

As shown in Figure 3-1, the manufacture of storage batteries is the major end use of lead (accounting for 81 percent of domestic lead use). About 63 percent of the total storage battery consumption is for manufacturing battery posts and grids, and 37 percent was for manufacturing lead oxides used in battery paste.<sup>16</sup>

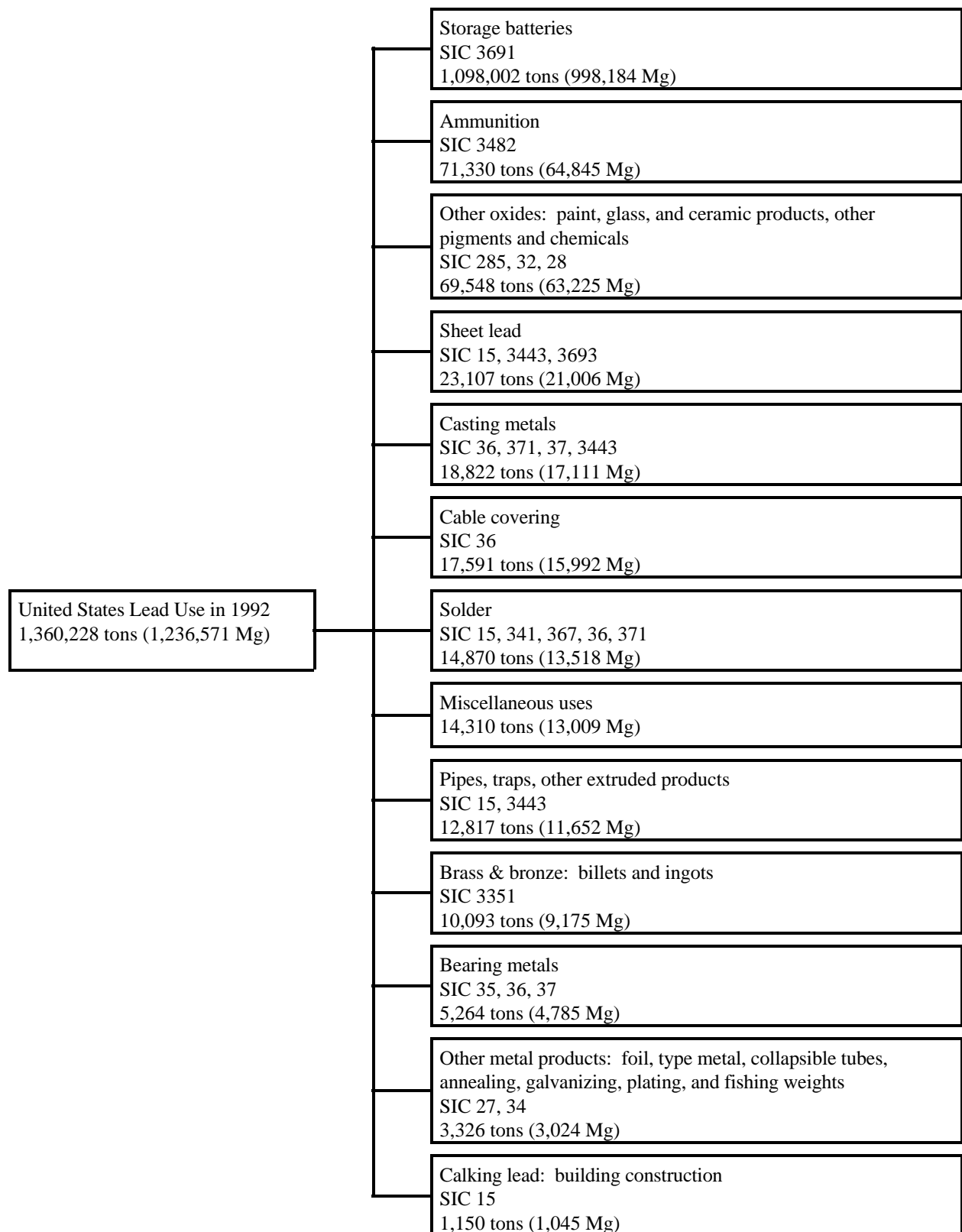


Figure 3-1. Consumption of Lead in the United States in 1992

Source: Reference 16.

The manufacture of ammunition and “other oxides” are the next largest uses of lead, each accounting for 5 percent of the total domestic lead consumption in 1992. “Other oxides” include the manufacture of pigments and chemicals, paints, glass, and ceramic products. The manufacture of pigments and chemicals account for 16 percent, and the manufacture of paints and glass and ceramics account for 84 percent of the total lead consumption for the “other oxides” category.<sup>16</sup>

The manufacture of casting materials, solder, sheet metal, and cable covering each accounted for 1 to 2 percent of total lead consumption in 1992.<sup>16</sup>

Some uses of lead experiencing increased growth over the past few years with continued growth expected are the use of lead in cathode ray tubes for television and computer screens (to protect viewer and service technicians from harmful radiation), and use of lead solder in the microelectronics industry.<sup>17</sup>

SECTION 4.0  
EMISSIONS OF LEAD AND LEAD COMPOUNDS FROM THE METALLURGICAL  
INDUSTRY

4.1 PRIMARY LEAD SMELTING

Lead is recovered from a sulfide ore, primary galena (lead sulfide), which also contains small amounts of copper, iron, zinc, and other trace elements. A description of the process used to manufacture lead and a discussion of the emissions resulting from the various operations are presented below.

A list of primary lead smelters currently in operation within the United States is given in Table 4-1. Primary lead smelters produced 449,800 tons (408,000 Mg) of refined lead in 1990.<sup>19</sup>

TABLE 4-1. DOMESTIC PRIMARY LEAD SMELTERS AND REFINERIES

Smelter	Refinery	1990 Production tons (Mg)
ASARCO, East Helena, MT	ASARCO, Omaha, NE	72,500 (65,800)
ASARCO, Glover, MO	Same site	123,200 (112,000)
Doe Run (formerly St. Joe), Herculaneum, MO	Same site	254,100 (231,000)

Source: Reference 19

#### 4.1.1 Process Description

Figure 4-1 presents a typical process flow diagram for primary lead smelting. The recovery of lead from the lead ore consists of three main steps: sintering, reduction, and refining.<sup>20</sup>

Sintering is carried out in a sintering machine, which is a large oven containing a continuous steel pallet conveyor belt. Each pallet consists of perforated grates, and beneath the grates are wind boxes, which are connected to fans to provide a draft through the moving sinter charge. Depending on the direction of the draft, the sinter machine is characterized as either an updraft or downdraft machine. Except for the draft direction, all machines are similar in design, construction, and operation. Capacities range from 1,000 to 2,500 tons (910 to 2,270 Mg) per day. Lead concentrates account for 30 to 35 percent of the input material for the sintering process. The balance of the charge consists of fluxes such as limestone and large amounts of recycled sinter or smelter residues.<sup>18</sup>

The blast furnace reduces the lead oxide produced in the sintering machine to elemental lead and removes undesirable impurities as a slag. Reduction reactions to elemental lead occur around 2,900°F (1,600°C). The resulting metal, called bullion, assays 94 to 98 percent lead. The furnace is a rectangular, water-cooled steel shell or shaft atop a refractory-lined crucible or hearth. Both sides are equipped with tuyeres through which pressurized combustion or blast air is introduced. Furnace capacities range from 500 to 1,000 tons (454 to 910 Mg) per day. The charge to the furnace includes sinter, coke, slags from dressing and refining processes, silica, limestone, and baghouse dust. About 80 percent of the charge consists of sinter that may contain from 28 to 50 percent lead. Blast air is introduced through the side-mounted tuyeres, resulting in partial combustion of coke and formation of carbon monoxide, and providing the heat required to reduce lead oxide to lead bullion.

Most of the impurities react with the silica and limestone and form a slag. The slag is skimmed continuously from the furnace and is treated either at the smelter or is shipped

Source: Reference 23.



elsewhere for recovery of the metal content. Slags that are high in zinc are generally treated at the smelter in a zinc forming furnace to recover zinc oxide.<sup>18</sup>

The lead bullion is tapped from the furnace periodically, and is usually treated in a drossing kettle before undergoing final refining. In the kettle, the bullion is cooled and the higher melting impurities, primarily copper, float to the surface and form a dross which is skimmed off and subsequently treated in a reverberatory furnace. The bullion undergoes a final refining in a series of cast iron kettles. The final lead product, typically 99.99 percent or more pure, is then cast into pigs or ingots for shipping.<sup>18</sup>

The function of the dross reverberatory furnace is to separate lead bullion carried over in the dross from other metals of economic value or contaminants in the dross. The dross lead content may be as high as 90 percent. Although much smaller, the reverberatory furnace used is similar in construction to the reverberatory furnace used in copper smelting. Where applied, end-products usually include lead bullion, which is recycled; matte, which is rich in copper and usually sent to a copper smelter for copper recovery; and speiss, which is high in arsenic and antimony.<sup>18</sup>

#### 4.1.2 Emission Control Techniques

Emission controls on primary lead smelter operations are used for controlling (PM) and sulfur dioxide (SO<sub>2</sub>) emissions resulting from the blast furnace and sintering machines. Centrifugal collectors (cyclones) may be used in conjunction with fabric filters or electrostatic precipitators (ESPs) for PM control. Because lead emissions generally are associated with PM emissions, devices used to control PM emissions should also control lead emissions. However, no data on the effectiveness of fabric filters and ESPs in controlling lead emissions are available.<sup>20</sup>

#### 4.1.3 Emissions

Lead can potentially be emitted from each unit operation within a primary lead smelting facility. Table 4-2 presents lead emission factors for specific primary lead operations. Since lead is generally emitted as PM, lead will be some fraction of total PM. The lead content of particulate emissions ranges from 20 to 65 percent. For blast furnaces, the lead content of total PM ranges from 10 to 40 percent. The lead content of particulate emissions from dross reverberatory furnaces ranges from 13 to 35 percent. For processes where the operating temperature is near the boiling point of lead, such as the sinter machine, lead fume may be emitted.

### 4.2 SECONDARY LEAD SMELTING

#### 4.2.1 Source Location

In 1990, primary and secondary smelters in the United States produced 1,380,000 tons (1,255,000 Mg) of lead. Secondary lead smelters produced 946,000 tons (860,000 Mg) or about 69 percent of the total refined lead produced in 1990.<sup>21</sup> Table 4-3 lists U.S. secondary lead smelters according to their annual lead production capacity.

#### 4.2.2 Process Description

The secondary lead smelting industry produces elemental lead and lead alloys by reclaiming lead, mainly from scrap automobile batteries. Blast, reverberatory, rotary, and electric furnaces are used for smelting scrap lead and producing secondary lead. Smelting is the reduction of lead compounds to elemental lead in a high-temperature furnace, which requires higher temperatures (2200 to 2300°F [1200 to 1260°C]) than those required for melting elemental lead (621°F [327°C]). Secondary lead may be refined to produce soft lead (which is nearly pure lead) or alloyed to produce hard lead. Most of the lead produced by secondary lead smelters is used in the production of lead-acid batteries.<sup>21</sup>

TABLE 4-2. LEAD EMISSION FACTORS FOR PRIMARY LEAD SMELTING FACILITIES

SCC	Emission Source	Control Device	Average Emission Factor in lb/ton (kg/Mg)	Emission Factor Range in lb/ton (kg/Mg)	Emission Factor Rating	Reference
3-03-010-02	Blast Furnace	None	$1.0 \times 10^{-4}$ ( $5.0 \times 10^{-5}$ ) <sup>a</sup>	---	U	22
		Baghouse	$6.7 \times 10^{-2}$ ( $3.4 \times 10^{-2}$ ) <sup>b</sup>	---	E	20
		Spray Tower/FF	$1.7 \times 10^{-2}$ ( $8.5 \times 10^{-3}$ ) <sup>a</sup>	---	U	22
3-03-010-04	Ore Crushing	None	$3.0 \times 10^{-1}$ ( $1.5 \times 10^{-1}$ ) <sup>c</sup>	---	U	23
		Baghouse	$2.0 \times 10^{-3}$ ( $1.0 \times 10^{-3}$ ) <sup>d</sup>	---	E	20
3-03-010-25	Sinter Machine Leakage	ESP/Scrubber	$3.2 \times 10^{-2}$ ( $1.6 \times 10^{-2}$ ) <sup>e</sup>	---	E	20
3-03-010-28	Tetrahedrite Drier	Baghouse	$6.0 \times 10^{-4}$ ( $3.0 \times 10^{-4}$ ) <sup>f</sup>	---	E	20
3-03-010-29	Sinter Machine (weak gas)	ESP/Scrubber	$1.9 \times 10^{-2}$ ( $9.5 \times 10^{-3}$ ) <sup>e</sup>	---	E	20
3-03-010-32	Ore Screening	Baghouse	$2.0 \times 10^{-3}$ ( $1.0 \times 10^{-3}$ ) <sup>f</sup>	---	E	20

<sup>a</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of lead produced.

<sup>b</sup> Emission factors are expressed in lb of pollutant emitted per ton bullion processed.

<sup>c</sup> Emission factors are expressed in lb of pollutant emitted per ton of ore crushed.

<sup>d</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of lead in ore.

<sup>e</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of sinter produced.

<sup>f</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of ore processed.

"---" means data not available.

TABLE 4-3. U.S. SECONDARY LEAD SMELTERS GROUPED ACCORDING TO ANNUAL LEAD PRODUCTION CAPACITY

Smelter	Location
<u>Small-Capacity Group:</u> <sup>a</sup>	
Delatte Metals <sup>b</sup>	Ponchatoula, LA
General Smelting and Refining Company	College Grove, TN
Master Metals, Inc. <sup>b</sup>	Cleveland, OH
Metals Control of Kansas <sup>b</sup>	Hillsboro, KS
Metals Control of Oklahoma <sup>b</sup>	Muskogee, OK
<u>Medium-Capacity Group:</u> <sup>c</sup>	
Doe Run Company	Boss, MO
East Penn Manufacturing Company	Lyon Station, PA
Exide Corporation	Reading, PA
GNB, Inc.	Columbus, GA
	Frisco, TX
Gulf Coast Recycling, Inc.	Tampa, FL
Refined Metals Corporation <sup>b</sup>	Beech Grove, IN
	Memphis, TN
RSR Corporation	City of Industry, CA
	Middletown, NY
Schuylkill Metals Corporation	Forest City, MO
Tejas Resources, Inc. <sup>b</sup>	Terrell, TX
<u>Large-Capacity Group:</u> <sup>d</sup>	
Exide Corporation	Muncie, IN
Gopher Smelting and Refining, Inc.	Eagan, MN
GNB, Inc.	Vernon, CA
RSR Corporation	Indianapolis, IN
Sanders Lead Company	Troy, AL
Schuylkill Metals Corporation	Baton Rouge, LA

Source: Reference 21, 24

<sup>a</sup> Less than 22,000 tons (20,000 Mg).

<sup>b</sup> These facilities were not operating as of January 1995.

<sup>c</sup> 22,000 to 82,000 tons (20,000 to 75,000 Mg).

<sup>d</sup> Greater than 82,000 tons (75,000 Mg).

Lead-acid batteries represent about 90 percent of the raw materials used at a typical secondary lead smelter, although this percentage may vary from one plant to the next. These batteries contain approximately 18-20 lb (8.2-9.1 kg) of lead per battery consisting of 40 percent lead alloys and 60 percent lead oxide. Other types of lead-bearing raw materials recycled by secondary lead smelters include drosses (lead-containing byproducts of lead refining), which may be purchased from companies that perform lead alloying or refining but not smelting; battery plant scrap, such as defective grids or paste; and scrap lead, such as old pipes or roof flashing. Other scrap lead sources include cable sheathing, solder, and babbitt-metal.<sup>21</sup>

As illustrated in Figure 4-2, the normal sequence of operations in a secondary lead smelter is scrap receiving, charge preparation, furnace smelting, lead refining, and alloying and casting. In the majority of plants, scrap batteries are first sawed or broken open to remove the lead alloy plates and lead oxide paste material. The removal of battery covers is typically accomplished using an automatic battery feed conveyor system and a slow-speed saw. Hammer mills or other crushing/shredding devices are then used to break open the battery cases. Float/sink separation systems are typically used to separate plastic battery parts, lead terminals, lead oxide paste, and rubber parts. The majority of lead smelters recover the crushed plastic materials for recycling. Rubber casings are usually landfilled or are incinerated in the smelting furnace for their fuel value, and in many cases, lead is reclaimed from the casings.

Paste desulfurization, an optional lead recovery step used by some secondary lead smelters, requires the separation of lead sulfate and lead oxide paste from the lead grid metal, polypropylene plastic cases, separators, and hard rubber battery cases. Paste desulfurization involves the chemical removal of sulfur from the lead battery paste. The process improves furnace efficiency by reducing the need for fluxing agents to reduce lead-sulfur compounds to lead metal. The process also reduces sulfur dioxide (SO<sub>2</sub>) furnace emissions. However, SO<sub>2</sub> emissions reduction is usually a less important consideration because many plants that perform paste desulfurization are also equipped with SO<sub>2</sub> scrubbers. About one-half of smelters perform paste desulfurization.<sup>21</sup>

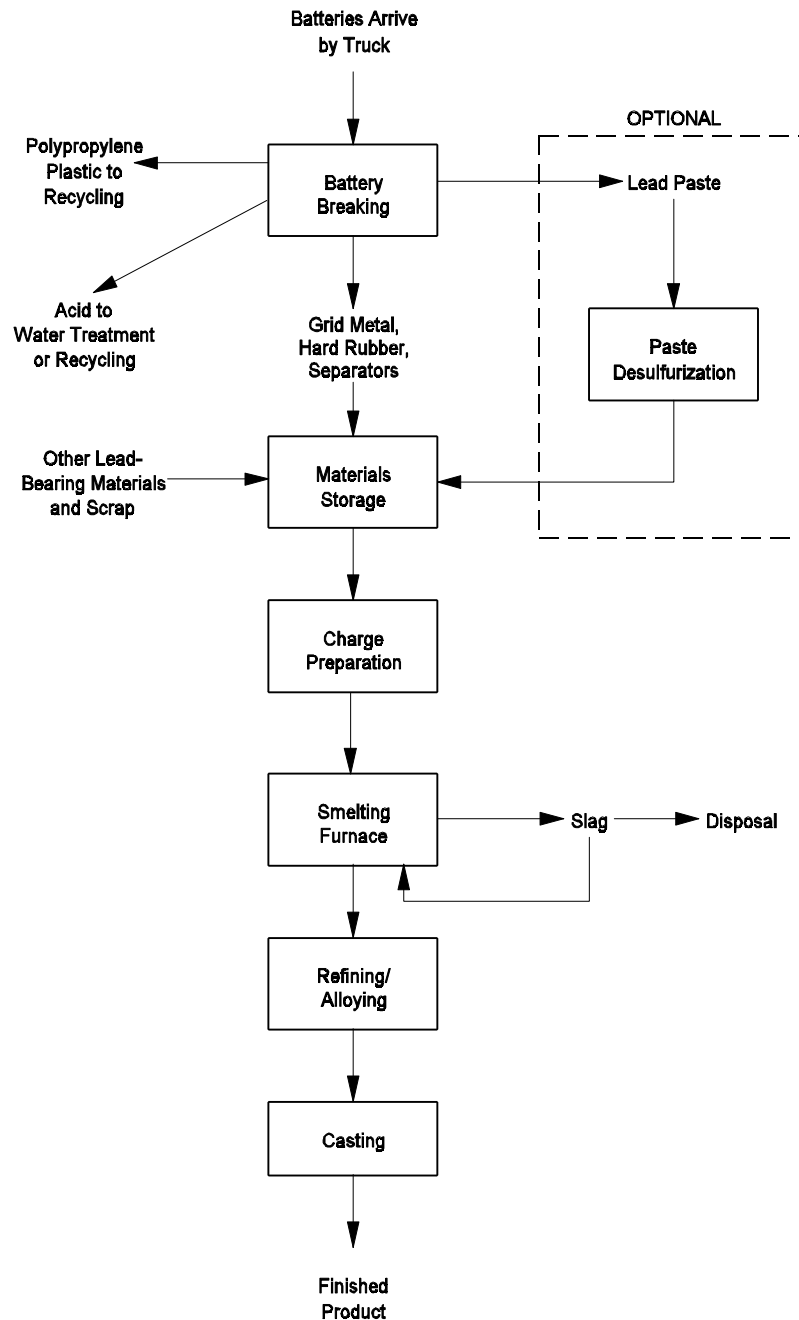


Figure 4-2. Simplified Process Flow Diagram for Secondary Lead Smelting

Source: Reference 21

After removing the lead components from the batteries, the lead scrap is combined with other charge materials, such as refining drosses and flue dust, and is charged to a reverberatory furnace. Reverberatory furnace slag, coke, limestone, sand, and scrap iron are fed to a blast, rotary or electric smelting furnace. Smelting furnaces are used to produce crude lead bullion, which is refined and/or alloyed into final lead products. In 1994, there were approximately 15 reverberatory furnaces, 24 blast furnaces, 5 rotary furnaces, and 1 electric furnace operating in the secondary lead industry in the United States.<sup>21</sup> Blast and reverberatory furnaces are currently the most common types of smelting furnaces used in the industry, although some new plants are using rotary furnaces.

### Reverberatory Furnaces

A reverberatory furnace (Figure 4-3) is a rectangular refractory-lined furnace operated on a continuous basis. Natural gas- or fuel oil-fired burners located at one end or at the sides of the furnace are used to heat the furnace and charge material to an operating temperature of about 2200 to 2300°F (1200 to 1260°C).<sup>21</sup> Oxygen enrichment may be used to decrease the combustion air requirements. Reverberatory furnaces are maintained at negative pressure by an induced draft fan.

Reverberatory furnace charge materials include battery grids and paste, battery plant scrap, rerun reverberatory furnace slag, flue dust, drosses, iron, silica, and coke. A typical charge over one hour may include 9.3 tons (8.4 Mg) of grids and paste to produce 6.2 tons (5.6 Mg) of lead.<sup>21</sup>

Charge materials are often fed to a natural gas- or oil-fired rotary drying kiln, which dries the material before it reaches the furnace. The temperature of the drying kiln is about 400°F (200°C), and the drying kiln exhaust is drawn directly into the reverberatory furnace or ventilated to a control device. From the rotary drying kiln, the feed is either dropped into the top of the furnace through a charging chute, or fed into the furnace at fixed intervals with a hydraulic ram. In furnaces that use a feed chute, a hydraulic ram is often used as a stoker to move the material down the furnace.

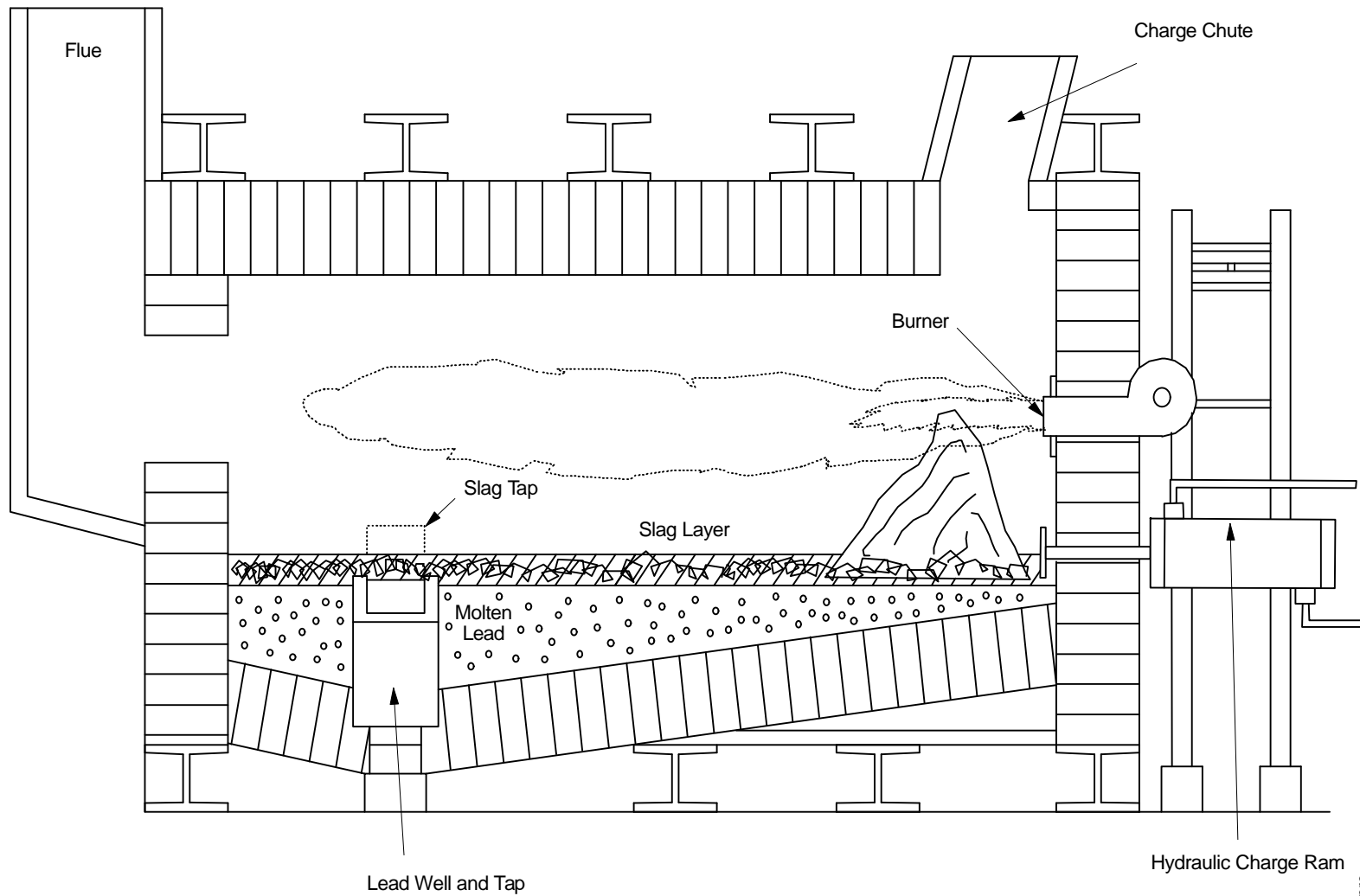


Figure 4-3. Cross-Sectional View of a Typical Stationary Reverberatory Furnace



Reverberatory furnaces are used to produce a soft, nearly pure lead product and a lead-bearing slag. This is done by controlling the reducing conditions in the furnace so that lead components are reduced to metallic lead bullion while the alloying elements (antimony, tin, arsenic) in the battery grids, posts, straps, and connectors are oxidized and removed in the slag. The reduction of  $\text{PbSO}_4$  and  $\text{PbO}$  is promoted by the carbon-containing coke added to the charge material:



The  $\text{PbSO}_4$  and  $\text{PbO}$  also react with the alloying elements to form lead bullion and oxides of the alloying elements, which are removed in the slag.

The molten lead collects in a pool at the lowest part of the hearth. Slag collects in a layer on top of this pool and retards further oxidation of the lead. The slag is made up of molten fluxing agents such as iron, silica, and lime, and typically has significant quantities of lead. Slag is usually tapped continuously and lead is tapped intermittently. The slag is tapped into a mould. The slag tap and crucible are hooded and vented to a control device. Reverberatory furnace slag usually has a high lead content (as much as 70 percent by weight) and is used as feed material in a blast or electric furnace to recover the lead. Reverberatory furnace slag may also be rerun through the reverberatory furnace during special slag campaigns before being sent to a blast or electric furnace. Lead may be tapped into a mold or directly into a holding kettle. The lead tap is usually hooded and vented to a control device.<sup>21</sup>

### Blast Furnaces

A blast furnace (Figure 4-4) is a vertical furnace that consists of a crucible with a vertical cylinder affixed to the top. The crucible is refractory-lined and the vertical cylinder consists of a steel water-jacket. Oxygen-enriched combustion air is introduced into the furnace through tuyeres located around the base of the cylinder.

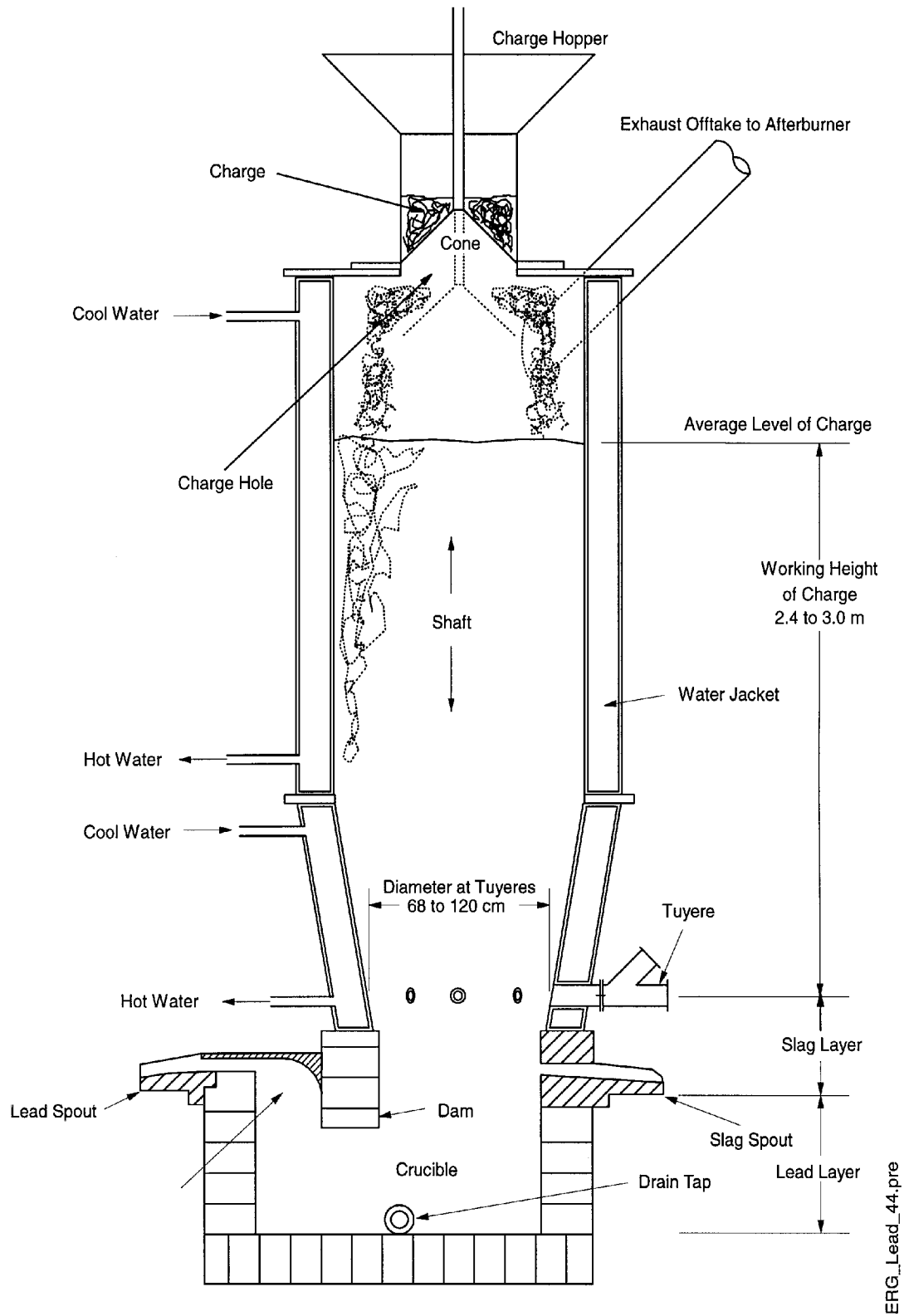


Figure 4-4. Cross-Section of a Typical Blast Furnace

Source: Reference 21.

Charge materials are pre-weighed to ensure the proper mixture and then are introduced into the top of the cylinder using a skip hoist, a conveyor, or a front-end loader. The charge fills nearly the entire cylinder. Charge material is added periodically to keep the level of the charge at a consistent working height while lead and slag are tapped from the crucible. Coke is added to the charge as the primary fuel, although natural gas jets may be used to start the combustion process. Combustion is self-sustaining as long as there is sufficient coke in the charge material. Combustion occurs in the layer of the charge nearest the tuyeres.

At plants that operate only blast furnaces, the lead-bearing charge materials may include broken battery components, drosses from the refining kettles, agglomerated flue dust, and lead-bearing slag. A typical charge over one hour may include 4.8 tons (4.4 Mg) of grids and paste, 0.3 tons (0.3 Mg) of coke, 0.1 tons (0.1 Mg) of calcium carbonate, 0.07 tons (0.06 Mg) of silica, 0.5 tons (0.4 Mg) of cast iron, and 0.2 tons (0.2 Mg) of rerun blast furnace slag, to produce 3.7 tons (3.4 Mg) of lead. At plants that also have a reverberatory furnace, the charge materials will also include lead-bearing reverberatory furnace slag.<sup>21</sup>

Blast furnaces are designed and operated to produce a hard (high alloy content) lead product by achieving greater furnace reduction conditions than those typically found in a reverberatory furnace. Fluxing agents include iron, soda ash, limestone, and silica (sand). The oxidation of the iron, limestone, and silica promotes the reduction of lead compounds and prevents oxidation of the lead and other metals. The soda ash enhances the reaction of  $\text{PbSO}_4$  and  $\text{PbO}$  with carbon from the coke to reduce these compounds to lead metal.

Lead tapped from a blast furnace has a higher content of alloying metals (up to 25 percent) than lead produced by a reverberatory furnace. In addition, much less of the lead and alloying metals is oxidized and removed in the slag, so the slag has a low metal content (e.g., 1 to 3 percent) and may qualify as a nonhazardous solid waste.

Because air is introduced into the blast furnace at the tuyeres, blast furnaces are operated at positive pressure. The operating temperature at the combustion layer of the charge is

between 2200 and 2600°F (1200 and 1400°C), but the temperature of the gases exiting the top of the charge material is only between 750 and 950°F (400 and 500°C).

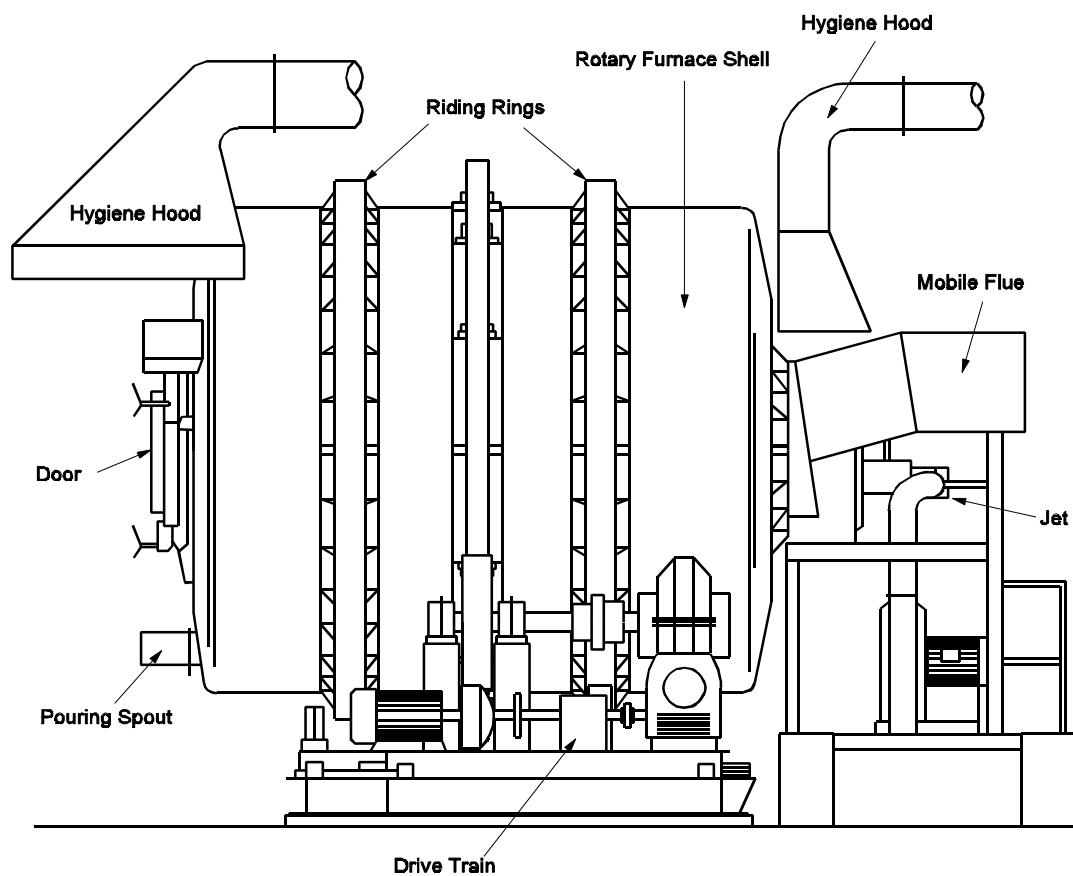
Molten lead collects in the crucible beneath a layer of molten slag. As in a reverberatory furnace, the slag inhibits the further oxidation of the molten metal. Lead is tapped continuously and slag is tapped intermittently, slightly before it reaches the level of the tuyeres. If the tuyeres become blocked with slag, they are manually or automatically "punched" to clear the slag. A sight glass on the tuyeres allows the furnace operator to monitor the slag level and ensure that the tuyeres are clear of slag. At most facilities, the slag tap is temporarily sealed with a clay plug, which is driven out to begin the flow of slag from the tap into a crucible. The slag tap and crucible are enclosed by a hood, which is vented to a control device.

A weir dam and siphon in the furnace are sometimes used to remove the lead from beneath the slag layer. Lead is tapped from a blast furnace into either a crucible or directly to a refining kettle designated as a holding kettle. The lead in the holding kettle is kept molten before being pumped to a refining kettle for refining and alloying. The lead tap on a blast furnace is hooded and vented to a control device.

### Rotary Furnaces

As noted previously in this section, rotary furnaces, sometimes referred to as rotary reverberatory furnaces, (see figure 4-5), are used at only a few recently constructed secondary lead smelters in the United States.<sup>21</sup> Rotary furnaces have two advantages over other furnace types: the ease of adjusting the relative amount of fluxing agents (because the furnaces are operated on a batch rather than a continuous basis), and better mixing of the charge materials.

A rotary furnace consists of a refractory-lined steel drum mounted on rollers with a variable-speed motor to rotate the drum. An oxygen-enriched natural gas or fuel oil jet at one end of the furnace heats the charge material and the refractory lining of the drum. The connection to the flue is located at the same end as the jet. A sliding door at the end of the



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Figure 4-5. Side View of a Typical Rotary Reverberatory Furnace

Source: Reference 21.

furnace opposite the jet allows charging of material to the furnace. Charge materials are typically placed in the furnace using a retractable conveyor or charge bucket, although other methods are possible.

Lead-bearing raw materials charged to rotary furnaces include broken battery components, flue dust, and drosses. Rotary furnaces can use the same lead-bearing raw materials as blast furnaces. They usually produce slag that is relatively free of lead, less than 2 percent. As a result, a blast furnace is not needed for recovering lead from slag, which can be disposed of as a nonhazardous waste.

Fluxing agents for rotary furnaces may include iron, silica, soda ash, limestone, and coke. The fluxing agents are added to promote the conversion of lead compounds to lead metal. Coke is used as a reducing agent rather than as a primary fuel. A typical charge may consist of 12 tons (11 Mg) of wet battery scrap, 0.8 tons (0.7 Mg) of soda ash, 0.6 tons (0.5 Mg) of coke, and 0.6 tons (0.5 Mg) of iron, and will yield approximately 9 tons (8 Mg) of lead product.<sup>21</sup>

The lead produced by rotary furnaces is a semi-soft lead with an antimony content somewhere between that of lead from reverberatory and blast furnaces. Lead and slag are tapped from the furnace at the conclusion of the smelting cycle. Each batch takes 5 to 12 hours to process, depending on the size of the furnace. Like reverberatory furnaces, rotary furnaces are operated at a slight negative pressure.

#### Electric Furnaces

An electric furnace consists of a large, steel, kettle-shaped container that is refractory-lined (Figure 4-6). A cathode extends downward into the container and an anode is located in the bottom of the container. Second-run reverberatory furnace slag is charged into the top of the furnace. Lead and slag are tapped from the bottom and side of the furnace, respectively. A fume hood covering the top of the furnace is vented to a control device.

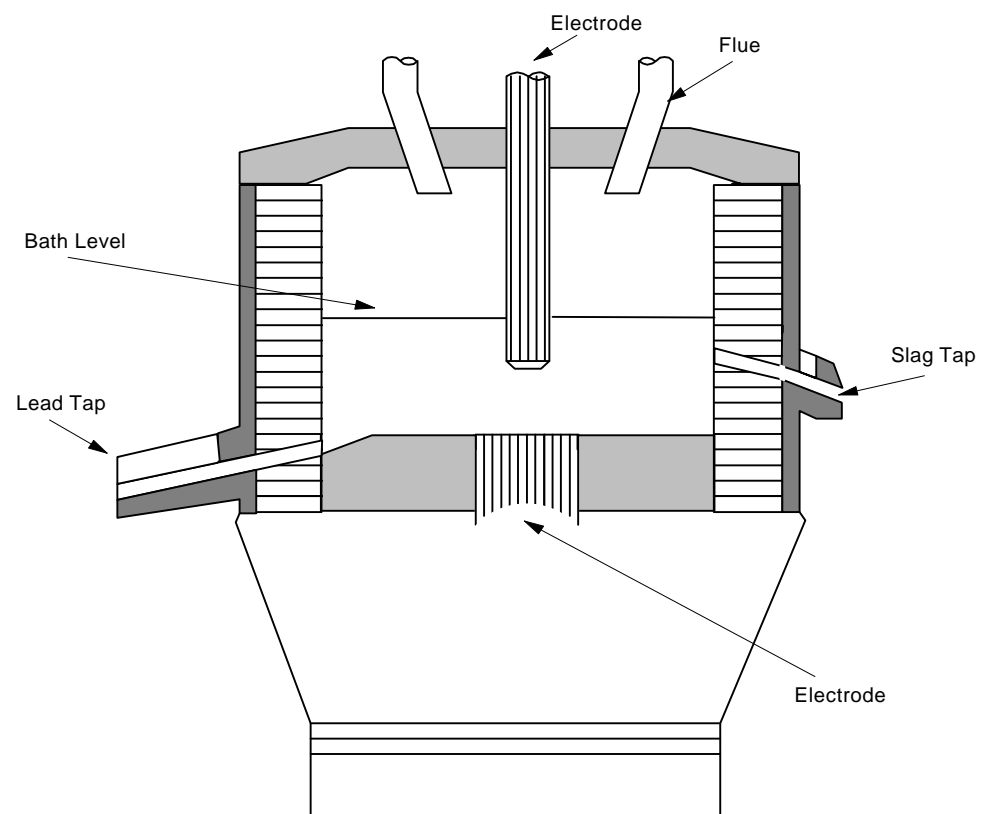


Figure 4-6. Cross-Sectional View of an Electric Arc Furnace for Processing Slag

In an electric furnace, electric current flows from the cathode to the anode through the scrap charge. The electrical resistance of the charge causes the charge to heat up and become molten. There is no combustion process involved in an electric furnace.

There is only one known electric furnace in operation in the United States for the secondary lead industry. It is used to process second-run reverberatory furnace slag, and it fulfills the same role as a blast furnace used in conjunction with a reverberatory furnace. However, the electric furnace has two advantages over a blast furnace. First, because there are no combustion gases, ventilation requirements are much lower than for blast or reverberatory furnaces. Second, the electric furnace is extremely reducing, and produces a glass-like, nearly lead-free slag that is nonhazardous .<sup>21</sup>

Refining, the final step in secondary lead production, consists of removing impurities and adding alloying metals to the molten lead obtained from the smelting furnaces to meet a customer's specifications. Refining kettles are used to purify and alloy molten lead.

#### 4.2.3 Emission Control Techniques

Three main strategies are used to control lead emissions and provide worker protection in secondary lead smelters. These three control strategies involve engineering measures, work practices, and personal protection. Engineering measures are the most effective means of lead emissions abatement. Included in this category are control devices, material substitution, process and equipment modification, isolation and automation, and local and general ventilation. Good work practices and personal hygiene have become important in reducing worker lead exposure. Included in these categories are housekeeping, administrative controls, and the use of personal protective equipment such as respirators, gloves, goggles, and aprons.<sup>25</sup>

Control devices used in secondary lead smelters include afterburners, baghouses, and scrubbers for furnace emissions control, and hooding and ventilation to a baghouse for process fugitive emissions control.<sup>26</sup>



#### 4.2.4 Emissions

In secondary lead smelting operations, lead is emitted in some degree from each unit operation. Measuring the level of lead in the blood of workers in each area is the most readily available method of determining the operations that contribute the most to lead emissions. Blood lead levels were highest among workers in the furnace area, clean-up area, welding operations area, and the alloying and sawing areas. The lowest blood lead levels were found in workers in the shipping area.<sup>25</sup>

Hazardous air pollutants and criteria air pollutants are emitted from secondary lead smelters as process emissions from the main smelting furnace exhaust, process fugitive emissions from smelting furnace charging and tapping and lead refining, and fugitive dust emissions from materials storage and handling and vehicle traffic. Lead emission factors for these processes are shown in Table 4-4.

The largest sources of process fugitive emissions are furnace charging, slag tapping, and agglomerating furnace operation. Lesser sources are lead tapping and kettle refining. Battery breaking and lead casting have fewer emissions. Lead casting is not a substantial source of emissions because the temperature of molten lead is well below the fuming temperature of lead.

Fugitive dust emissions contain lead emissions but are dependent upon the size of the facility and the fugitive dust controls and practices in place at each facility. These emissions cannot be measured and can only be roughly estimated using emission factors and facility specific data.<sup>21</sup>

TABLE 4-4. LEAD EMISSION FACTORS FOR SECONDARY LEAD SMELTING

SCC Number	Emission Source	Control Device	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
3-04-004-03	Blast Furnace (Cupola)	None	1.04x10 <sup>2</sup> (5.2x10 <sup>1</sup> )	6.4x10 <sup>1</sup> - 1.4x10 <sup>2</sup> (3.1x10 <sup>1</sup> - 7.0x10 <sup>1</sup> )	C	28
		Wet Scrubber/FF/ Cyclone/Settling Chamber/Demister	2.9x10 <sup>-1</sup> (1.5x10 <sup>-1</sup> )	3.0x10 <sup>-2</sup> - 6.4x10 <sup>-1</sup> (2.0x10 <sup>-2</sup> - 3.2x10 <sup>-1</sup> )	C	28
3-04-004-04	Rotary Sweating Furnace	None	---	7.0 - 1.6x10 <sup>1</sup> (4.0 - 8.0)	E	28
		Baghouse	2.8x10 <sup>-2</sup> (1.4x10 <sup>-2</sup> )	1.6x10 <sup>-2</sup> - 5.2x10 <sup>-2</sup> (8.0x10 <sup>-3</sup> - 2.6x10 <sup>-2</sup> )	D	29
		Baghouse/scrubber	1.9x10 <sup>-2</sup> (9.5x10 <sup>-3</sup> )	1.7x10 <sup>-2</sup> - 2.1x10 <sup>-2</sup> (8.5x10 <sup>-3</sup> - 1.1x10 <sup>-2</sup> )	D	29
3-04-004-13	Smelting Furnace Fugitives	None	---	2.0x10 <sup>-1</sup> - 6.0x10 <sup>-1</sup> (1.0x10 <sup>-1</sup> - 3.0x10 <sup>-1</sup> )	E	28
		Baghouse	1.2x10 <sup>-2</sup> (6.0x10 <sup>-3</sup> )	7.4x10 <sup>-3</sup> - 2.1x10 <sup>-2</sup> (3.7x10 <sup>-3</sup> - 1.1x10 <sup>-2</sup> )	U	30
3-04-004-02	Reverberatory Furnace	None	6.5x10 <sup>1</sup> (3.3x10 <sup>1</sup> )	3.5x10 <sup>1</sup> - 9.7x10 <sup>1</sup> (1.7x10 <sup>1</sup> - 4.8x10 <sup>1</sup> )	C	28
3-04-004-26	Kettle Refining	None	1.0x10 <sup>-2</sup> (6.0x10 <sup>-3</sup> )	---	C	28
3-04-004-14	Kettle Refining Fugitives	None	6.00x10 <sup>-4</sup> (3.00x10 <sup>-4</sup> )	---	E	28
		Afterburner/FF/ Venturi Scrubber/ Demister	2.4 (1.2)	---	U	22

TABLE 4-4. LEAD EMISSION FACTORS FOR SECONDARY LEAD SMELTING (CONTINUED)

SCC Number	Emission Source	Control Device	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
3-04-004-09	Casting	None	$1.0 \times 10^{-2}$ ( $5.0 \times 10^{-3}$ )	---	C	28
3-04-004-25	Casting Fugitives	None	$7.0 \times 10^{-4}$ ( $3.5 \times 10^{-4}$ )	---	E	28

<sup>a</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of lead produced.

"---" means data not available.

FF = Fabric Filter.

## 4.3 PRIMARY COPPER PRODUCTION

### 4.3.1 Source Description

Seven primary copper smelters were operating in the United States in 1995 and one additional was closed for modifications.<sup>27</sup> The combined production capacity in 1995 for the seven plants in operation was 1,728,043 tons (1,570,623 Mg).

### 4.3.2 Process Description

The pyrometallurgical process used to extract copper from sulfide ore concentrates is based upon copper's strong affinity for sulfur and its weak affinity for oxygen as compared to that of iron and other base metals in the ore. The purpose of smelting is to separate the copper from the iron, sulfur, and commercially worthless mineral materials. All eight of the primary copper smelters currently produce anode copper from sulfur-bearing ores with the same basic processes:

- matte smelting;
- converting; and
- refining in an anode furnace.

Copper concentrates received by the smelter typically contain 24 to 30 percent copper, 30 percent sulfur, 25 percent iron, and 10 to 20 percent oxides of silicon, calcium, aluminum, magnesium, and zinc. (Copper-bearing ores typically contain 0.5 to 1 percent copper by mass. A froth-flotation process is utilized to produce the "concentrate." This froth-flotation process may or may not be performed at the smelter site.) Concentrates also contain input impurities, such as lead, arsenic, antimony, cadmium, chromium, cobalt, manganese, mercury, nickel, and selenium. These input impurities are typically found in combined concentrations of less than one percent. The smelter may also receive copper scrap (for direct input into the converters), or may receive other non-concentrate inputs, such as precipitates, or copper "speiss."

Incoming concentrates are typically dried before input into a smelting furnace or reactor. Several types of smelting furnaces/reactors are currently utilized in the United States, including flash furnaces, CONTOP reactors, Noranda reactors, and IsaSmelt reactors.

Figure 4-7 illustrates basic smelting operations.

The smelting furnace/reactor produces molten copper matte, typically containing 55-75 percent copper, which is tapped from the furnace, and transferred by ladles to converters. The smelting furnace/reactors also produces slag, containing relatively low amounts of copper (typically less than two percent). This slag may be discarded directly, if less than 1 percent copper, or may be transferred to an electric slag-cleaning vessel (for further copper removal), or may be cooled and reconcentrated (in an attempt for further copper removal).

Molten copper matte is transferred by ladles from the furnace/reactor, and poured into the converters. In the converters, further sulfur is removed from the matte, and in addition, iron is oxidized and separated by skimming. The output from the converters is "blister" copper, generally containing greater than 98 percent copper. Figure 4-8 illustrates a typical converter.

Molten blister copper is poured from the converter, and transferred by ladles to anode furnaces, where further refining by removal of oxygen and other impurities takes place. The resulting "anode" copper is generally greater than 98.5 percent pure. It is cast into anodes for use in the final electrolytic refining step.

Further refining of "anode" copper into "cathode" copper (greater than 99.9 percent purity) is performed by electrolytic means in a "tank house." Production of cathode copper may or may not take place at the smelter site.

#### 4.3.3 Emissions

Particulate matter and SO<sub>2</sub> are the principal air contaminants emitted from primary copper smelters. Actual emissions from a particular smelter will depend upon the smelting configuration (type and mix of equipment used), control devices applied, and the

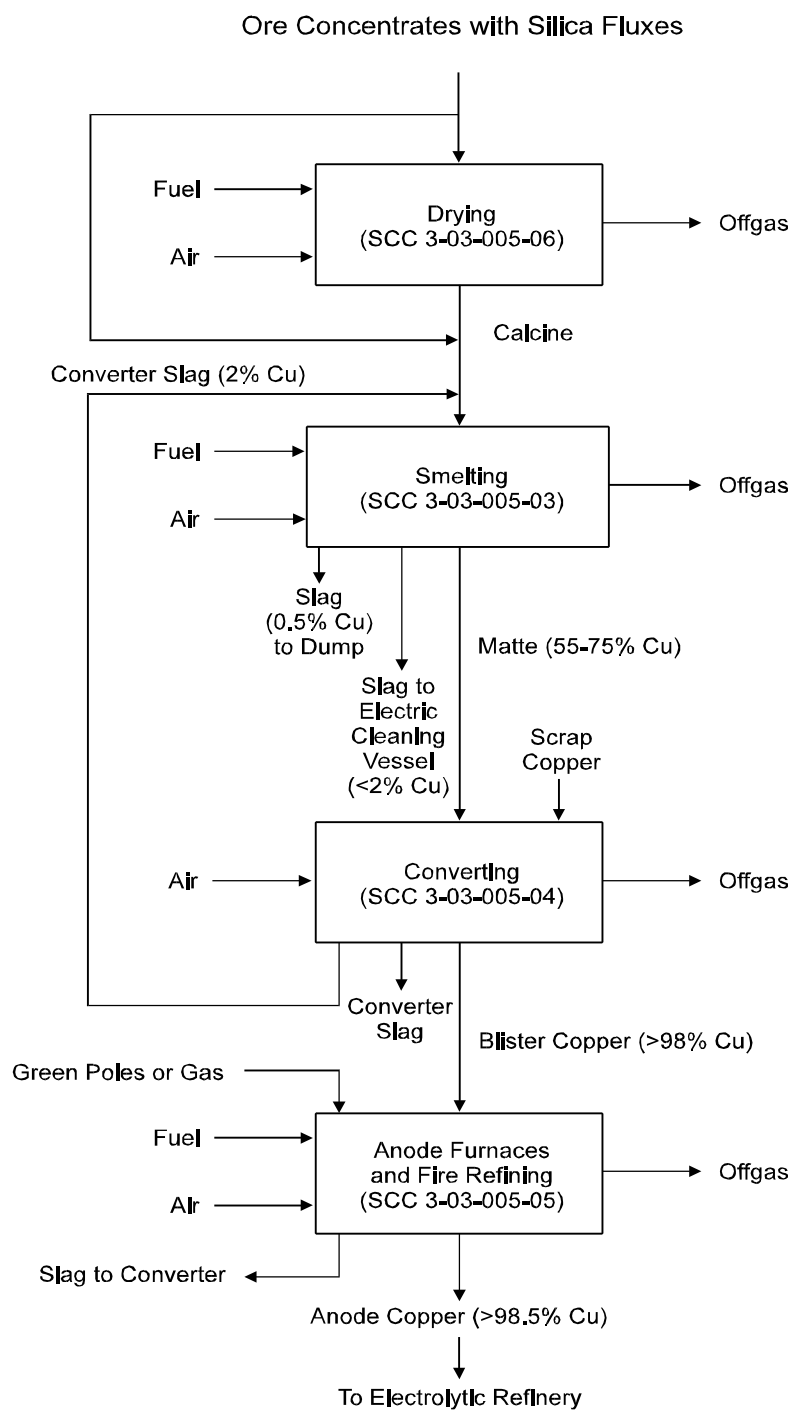


Figure 4-7. Typical Primary Copper Smelter Flowsheet

Source: Reference 27.

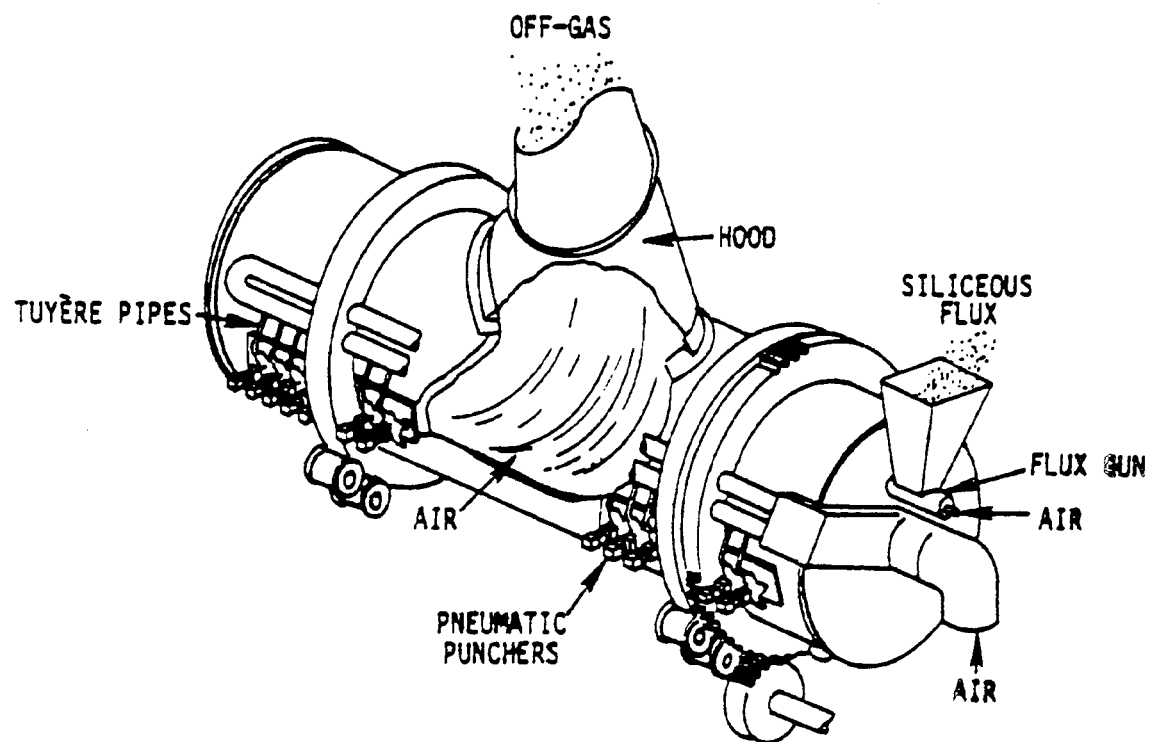


Figure 4-8. Copper Converter

Source: Reference 31.

operating and maintenance practices employed. Typically, lead will be emitted as PM. In addition, actual lead emissions will vary depending on the quantity of lead introduced to the smelter with the copper-bearing feed materials. The available emission factors for smelting and converting are presented in Table 4-5. No factors are available for refining.

In addition to process emissions, significant quantities of fugitive emissions are also generated during material handling operations and furnace charging and tapping. Fugitive particulates emitted from primary copper smelting consist primarily of metallic oxides and dust. Major sources of fugitive emissions are shown in Figure 4-9. Principal sources include ore concentrate unloading and handling, calcine transfer operations, furnace tapping operations, and converter charging and skimming operations. Information on chemical characteristics of fugitive particulate, including lead content, from a variety of these sources is presented in Table 4-6. The data illustrated in the table suggest that the principal source of fugitive lead emissions may be the converters, with fugitive particulate emissions containing 2 to 6 percent lead.<sup>18</sup>

#### 4.3.4 Emission Control Techniques

Control devices for particulate emissions from smelting and converting operations typically consist of a dry (plate/wire) ESP, baghouses, scrubbers, and a wet (tube/wire) acid mist ESP (to remove sulfuric acid and volatile heavy metals that condense during the cooling process).

The control techniques applied vary depending on smelter configuration, process equipment mix, emissions characteristics, and feasibility for SO<sub>2</sub> control. Off-gases from smelting equipment that produce relatively high concentrations of SO<sub>2</sub> (greater than 4 percent; includes fluidized-bed roasters, non-reverberatory smelting furnaces, and converters) are generally treated in single- or double-contact sulfuric acid plants for SO<sub>2</sub> removal.



TABLE 4-5. LEAD EMISSION FACTORS FOR PRIMARY COPPER SMELTING FACILITIES

SCC Number	Emission Source	Control Device	Average Emission Factor <sup>a</sup> in lb/ton (kg/Mg)	Emission Factor Rating
3-03-005-03	Smelting	None	$7.2 \times 10^{-2}$ ( $3.0 \times 10^{-2}$ )	C
3-03-005-04	Converter	None	$2.7 \times 10^{-1}$ (0.135)	C

Source: Reference 32

<sup>a</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of concentrated ore processed and represent total process and fugitive emissions.

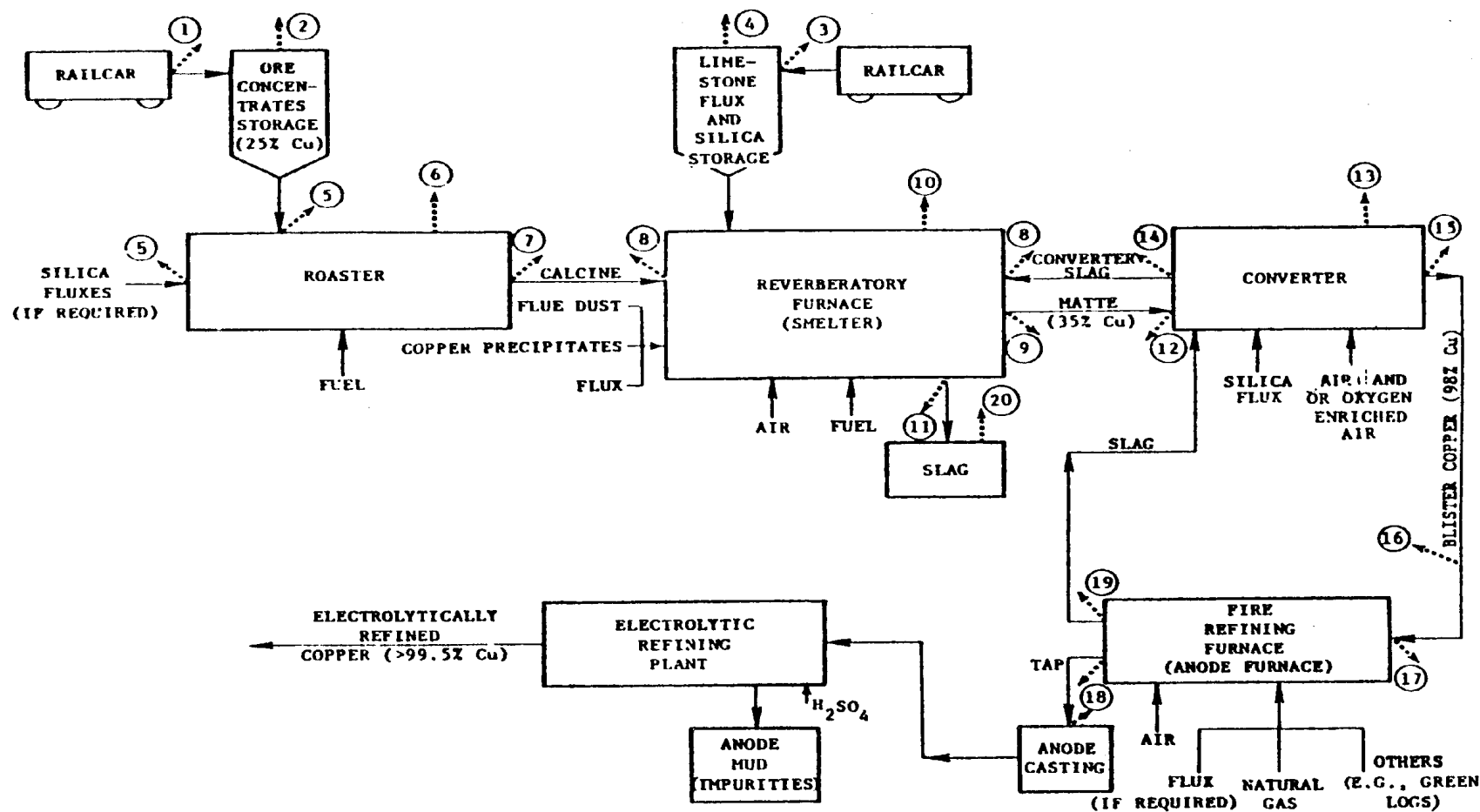


Figure 4-9. Fugitive Emission Sources at Primary Copper Smelters

Source: Reference 27.

TABLE 4-6. CHEMICAL CHARACTERISTICS OF FUGITIVE PARTICULATE EMISSIONS FROM VARIOUS SOURCES AT PRIMARY COPPER SMELTERS

Process Step	Composition (%)							
	Cu	Fe	S	SiO <sub>2</sub>	Zn	Cd	Pb	Other
Ore concentrate storage and handling	28	24	32	11			0.3	5
Slag handling	0.5	40	1.5	38			0.3 - 18	20
Roaster loading and operation	5				16		0.3 - 18	0.5
Reverberatory furnace loading and operation	5				16		0.4 - 18	0.5
Matte transfer	42	32	25	1			0.25	
Converter loading and blowing	1				8	4	2 - 6	

Source: Reference 18

Fugitive emissions produced by the majority of smelter fugitive sources, including ore concentrate handling, calcine transfer, and furnace tapping (matte and slag), are controlled by enclosing the fugitive emission points in a hood and exhausting the captured emissions to a control device for collection. Fugitive emissions associated with converter operations are much more difficult to control. These emissions are substantial and occur during charging, skimming, or pouring operations when the converter mouth is rotated out from under the primary hood. They also result from primary hood leakage. Control techniques for converter fugitive emissions include secondary hoods of various designs and ventilating the converter building to a control device. All plants currently operating have hooding at all smelting furnace/vessel matte and slag tapping points. Six of the eight plants in operation have both primary and secondary hoods on Pierce-Smith converters.<sup>27</sup>

## 4.4 SECONDARY COPPER PRODUCTION

### 4.4.1 Source Description

The secondary copper industry processes scrap metals to recover copper. Products include refined copper or copper alloys in forms such as ingots, wirebar, anodes, and shot. Copper alloys are combinations of copper and other materials, commonly tin, zinc, and lead. Also, for special applications, combinations include such metals as cobalt, manganese, iron, nickel, cadmium, and beryllium, and non-metals such as arsenic and silicon. A list of secondary copper smelters currently operating within the United States is provided in Table 4-7. Secondary copper capacity totaled 529,100 tons (479,000 Mg) in 1992.<sup>33</sup> Except where otherwise indicated, this section is derived from Section 12.9 of AP-42.<sup>34</sup>

### 4.4.2 Process Description

The principal processes involved in copper recovery are scrap metal pretreatment and smelting. Pretreatment includes cleaning and concentration to prepare the material for the smelting furnace. Smelting involves heating and treating the scrap to achieve separation and purification of specific metals.

The feed material used in the recovery process can be any metallic scrap containing a useful amount of copper, bronze (copper and tin), or brass (copper and zinc). Traditional forms are punchings, turnings and borings, defective or surplus goods, metallurgical residues such as slags, skimmings, and drosses, and obsolete, worn-out, or damaged articles, including automobile radiators, pipe, wire, bushings, and bearings.

The type and quality of the feed material determines the processes the smelter will use. Due to the large variety of feed materials available, the method of operation varies greatly among plants. Generally, a secondary copper facility deals with less pure raw materials and produces a more refined product, whereas brass and bronze alloy processors take cleaner scrap

TABLE 4-7. DOMESTIC SECONDARY COPPER PRODUCERS

Smelter	1992 Capacity, tons (Mg)
Cerro Copper Products, Sauget, IL	77,000 (70,000)
Chemetco (Concorde Metals), Alton, IL	148,000 (135,000)
Franklin Smelting and Refining, Philadelphia, PA	17,600 (16,000)
Gaston Recycling Industries, Gaston, SC	121,000 (110,000)
Scrapwire Co., Carrolton, GA	115,500 (105,000)
Cyprus Casa Grande Corp., Lakeshore, AZ	49,500 (45,000)

Source: Reference 33

and do less purification and refining. Figure 4-10 is a flowsheet depicting the major processes that can be expected in a secondary copper-smelting operation.

Pretreatment of the feed material can be accomplished using several different procedures, either separately or in combination. Feed scrap is concentrated by manual and mechanical methods, such as sorting, stripping, shredding, and magnetic separation. Feed scrap is sometimes briquetted in a hydraulic press. Pyrometallurgical pretreatment may include sweating, burning off insulation (especially from wire scrap), and drying (burning off oil and volatiles) in rotary kilns. Hydrometallurgical methods include floatation and leaching, with chemical recovery.

In smelting, low-grade scrap is smelted in a cupola furnace, producing "black copper" (70 to 80 percent Cu) and slag; these are often separated in a reverberatory furnace. From here, the melt is transferred to a converter or electric furnace to produce "blister" copper, which is 90 to 99 percent Cu. The actual temperature at which the smelting takes place is not known. However, the operating temperatures are probably not significantly different from that of primary copper-smelting operations (1200°F [650°C]).

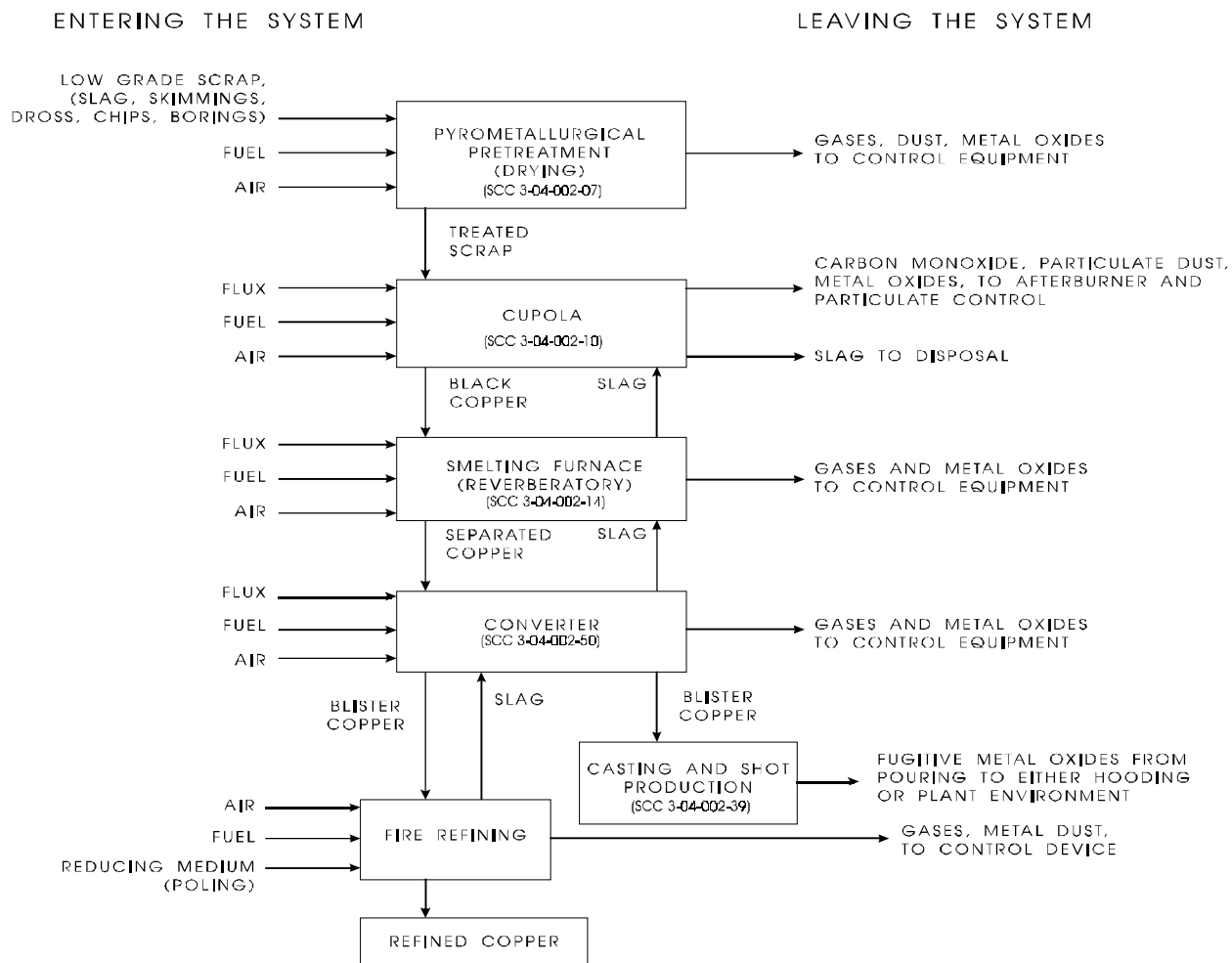


Figure 4-10. Secondary Copper Smelting Processes

Blister copper may be poured to produce shot or castings, but is often further refined electrolytically or by fire refining. The fire-refining process is essentially the same as that described for the primary copper-smelting industry. The sequence of events in fire refining is the following: (1) charging, (2) melting in an oxidizing atmosphere, (3) skimming the slag, (4) blowing with air or oxygen, (5) adding fluxes, (6) "poling" or otherwise providing a reducing atmosphere, (7) reskimming, and (8) pouring.

To produce bronze or brass, rather than copper, an alloying operation is required. Clean, selected bronze and brass scrap is charged to a melting furnace with alloying metals to bring the resulting mixture to the desired final composition. Fluxes are added to remove impurities and to protect the metal against oxidation by air. Air or oxygen may be blown through the melt to adjust the composition by oxidizing excess zinc.

With zinc-rich feed, such as brass, the zinc oxide concentration in the exhaust gas is sometimes high enough to make recovery for its metal value desirable. This process is accomplished by vaporizing the zinc from the melt at high temperatures and then capturing the oxide downstream in a process fabric filter.

The final step is always casting the alloyed or refined metal into a desired form, e.g., shot, wirebar, anodes, cathodes, ingots, or other cast shapes. The metal from the melt is usually poured into a ladle or a small pot (which serves as a surge hopper and a flow regulator) and then continues into a mold.

#### 4.4.3 Emission Control Techniques

The principal pollutant emitted from secondary copper smelting activities is PM in various forms. Removing insulation from wire by burning produces particulate emissions of metal oxides and unburned insulation. Drying chips and borings to remove excess oils and cutting fluids can result in large amounts of dense smoke consisting of soot and unburned hydrocarbons. Particulate emissions from the top of a cupola furnace consist of metal oxide fumes, dirt, and dust from limestone and coke.

The smelting process uses large volumes of air to oxidize sulfides, zinc, and other undesirable constituents of the feed. This procedure generates considerable particulate matter in the exhaust gas stream. The wide variation among furnace types, charge quality, extent of pretreatment, and size of the charge is reflected in a broad spectrum of particle sizes and variable grain loadings in the exhaust gases. One major factor contributing to differences in emission rates is the amount of zinc present in scrap feed materials; due to its low boiling point, zinc evaporates and combines with oxygen, producing zinc oxide fumes.

Metal oxide fumes from furnaces used in secondary copper smelters may be controlled by fabric filters, ESPs, or wet scrubbers. Control efficiency by fabric filters may be higher than 99 percent, but cooling systems are needed to prevent the hot gases from damaging or destroying the bag filters. A two-stage system using both water jacketing and radiant cooling is common. Electrostatic precipitators are not as well suited to this application, having a low-collection efficiency for dense particulates, such as oxides of lead and zinc. Wet scrubber installations also are relatively ineffective in the secondary copper industry. Scrubbers are useful mainly for particles larger than 1 micron, but the metal oxide fumes are generally submicron in size.

Particulate emissions associated with drying kilns can be similarly controlled. Drying temperatures up to 302°F (150°C) produce relatively cool exhaust gases, requiring no precooling for control by fabric filters.

Wire burning generates large amounts of particulate matter, primarily unburned combustibles. These emissions can be effectively controlled by direct-flame afterburners, with an efficiency of 90 percent or better if the afterburner combustion temperature is maintained above 1,800°F (1,000°C). If the insulation contains chlorinated organics, such as polyvinyl chloride, hydrogen chloride gas will be generated and will not be controlled by the afterburner.

One source of fugitive emissions in secondary smelter operations is charging scrap into furnaces containing molten metals. This often occurs when the scrap being processed is not sufficiently compacted to allow a full charge to fit into the furnace prior to heating. The



introduction of additional material onto the liquid metal surface produces significant amounts of volatile and combustible materials and smoke, which can escape through the charging door. Briquetting the charge offers a way to avoid fractional charges. When fractional charging cannot be eliminated, fugitive emissions are reduced by shutting off the furnace burners during charging. This reduces the flow of exhaust gases and enhances the ability of the exhaust control system to handle the emissions.

Metal oxide fumes are generated not only during melting, but also during pouring of the molten metal into the molds. Other dusts may be generated by the charcoal, or other lining used in association with the mold. Covering the metal surface with ground charcoal is a method used to make "smooth-top" ingots. This process creates a shower of sparks, releasing emissions into the plant near the furnace and the molds being filled.

#### 4.4.4 Emissions

Lead may be present in the scrap metals that are processed to recover secondary copper, therefore, lead emissions can be expected from secondary copper-smelting operations. Generally, lead will be emitted as particulate matter. Lead emission factors are presented in Table 4-8.

### 4.5 PRIMARY ZINC SMELTING

#### 4.5.1 Source Description

Zinc is found primarily as the sulfide ore sphalerite (ZnS). Its common coproduct ores are lead and copper. Metal impurities commonly associated with ZnS are cadmium and minor quantities of germanium, gallium, indium, and thallium.<sup>35</sup>

Four primary zinc smelters were in operation in the United States in 1992. Three of the smelters employed the electrolytic smelting process and one employed a pyrometallurgical

TABLE 4-8. LEAD EMISSION FACTORS FOR SECONDARY COPPER SMELTING FACILITIES

SCC Number	Emission Source	Control Device	Average Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
3-04-002-42	Reverberatory Furnace (charge with other alloy [7%])	None	5.0 (2.5)	---	B	34
3-04-002-43	Reverberatory Furnace (charge with high lead [58%])	None	5.0x10 <sup>1</sup> (2.5x10 <sup>1</sup> )	---	B	34
3-04-002-44	Reverberatory Furnace (charge with red/yellow brass)	None	1.32x10 <sup>1</sup> (6.6)	---	B	34
3-04-002-xx	Secondary Copper - smelting	Baghouse	1.00x10 <sup>-3</sup> (5.00x10 <sup>-4</sup> ) <sup>b</sup>	---	B	37

<sup>a</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of product, except as noted.

<sup>b</sup> Emission factor is expressed in lb (kg) of pollutant emitted per ton (Mg) of material processed.

"---" means data not available.

process. Table 4-9 lists the four U.S. smelters according to their process type and slab zinc production.<sup>36</sup>

#### 4.5.2 Process Description

A general diagram of the electrolytic process is presented in Figure 4-11. Electrolytic processing involves four major steps: roasting, leaching, purification, and electrolysis.

Roasting is common to both electrolytic and pyrometallurgical processing. Calcine is produced by the roasting reactions in any one of three types of roasters: multiple-hearth, suspension, or fluidized-bed. Multiple-hearth roasters are the oldest technology; fluidized-bed roasters are the most modern. Fluidized-bed roasters are currently the only type of roasting process used in the United States. The primary zinc-roasting reaction occurs between 1,184 and 1,832°F (640 and 1,000°C), depending on the type of roaster used. The reaction is the following:

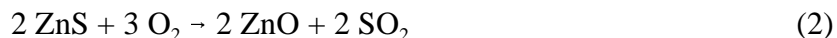


TABLE 4-9. DOMESTIC PRIMARY ZINC PRODUCERS

Company	Type of Process	1992 Slab Zinc Production Capacity, ton (Mg)
Big River Zinc Co., Sauget, IL	Electrolytic	90,200 (82,000)
Jersey Miniers Zinc Co., Clarksville, TN	Electrolytic	107,800 (98,000)
Zinc Corporation of America, Bartlesville, OK	Electrolytic	56,100 (51,000)
Zinc Corporation of America, Monaca, PA	Pyrometallurgical	135,300 (123,000)

Source: Reference 36

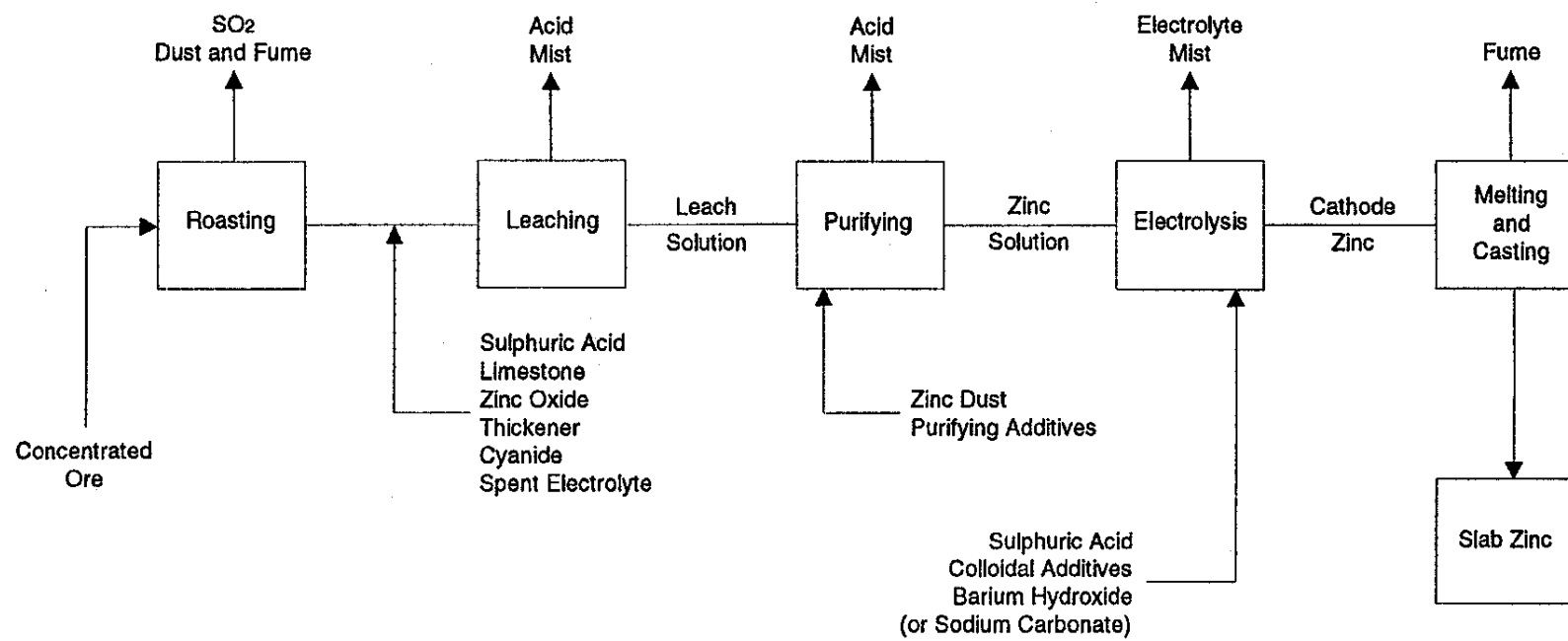


Figure 4-11. Electrolytic Primary Zinc-Smelting Process

Source: Reference 35.

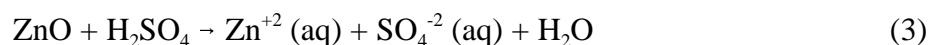
In a multiple-hearth roaster, the concentrate is blown through a series of nine or more hearths stacked inside a brick-lined cylindrical column. As the feed concentrate drops through the furnace, it is first dried by the hot gases passing through the hearths and then oxidized to produce calcine. The reactions are slow and can only be sustained by the addition of fuel.

In a suspension roaster, the feed is blown into a combustion chamber, which is very similar to that of a pulverized coal furnace. Additional grinding, beyond that required for a multiple-hearth furnace, is normally required to ensure that heat transfer to the material is fast enough to initiate desulfurization and oxidation reactions in the furnace chamber. Hearths at the bottom of the roaster capture the larger particles, which need more time in the furnace to complete the reactions.

In a fluidized-bed roaster, finely ground sulfide concentrates are suspended and oxidized within a pneumatically supported feedstock bed. This technique achieves the lowest sulfur content calcine of the three roaster designs.

Suspension and fluidized-bed roasters are superior to multiple-hearth roasters for several reasons. Although they emit more particulate, their reaction rates are much faster, allowing greater process rates. Also, the SO<sub>2</sub> content of the effluent streams of these two roasters is significantly higher, permitting more efficient and economical use of acid plants to control SO<sub>2</sub> emissions.

Leaching is the first step of electrolytic reduction. In this step, the zinc oxide reacts with sulfuric acid to form aqueous zinc sulfate in an electrolytic solution.

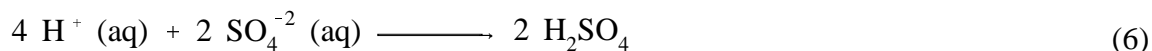
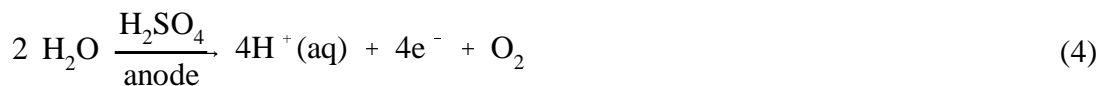


Single- and double-leach methods can be used, although the former exhibits excessive sulfuric acid losses and poor zinc recovery. In double leaching, the calcine is first leached in a neutral solution. The readily soluble sulfates from the calcine dissolve, but only a

portion of the zinc oxide enters the solution. The calcine is then leached in the acidic electrolysis recycle electrolyte. The zinc oxide is dissolved as shown in reaction (3), as are many of the impurities, especially iron. The electrolyte is neutralized by this process and it serves as the leach solution for the first stage of calcine leaching. This recycling also serves as the first stage of refining because much of the dissolved iron precipitates out of the solution. Variations on this basic procedure include the use of progressively stronger and hotter acid baths to bring as much of the zinc into solution as possible.

Purification is a process in which a variety of reagents are added to the zinc-laden electrolyte to force impurities to precipitate. The solid precipitates are separated from the solution by filtration. The techniques that are used are among the most advanced industrial applications of inorganic solution chemistry. Processes vary from smelter to smelter and the details are proprietary and often patented. Metallic impurities such as arsenic, antimony, cobalt, germanium, nickel, and thallium interfere severely with the electrolytic deposition of zinc, and their final concentrations are limited to less than  $4 \times 10^{-7}$  lb/gal (0.05 mg/L).

Electrolysis takes place in tanks, or cells, containing a number of closely spaced rectangular metal plates that act as anodes (made of lead with 0.75 to 1.0 percent silver) and as cathodes (made of aluminum). A series of three major reactions occurs within the electrolysis cells:



Oxygen gas is released at the anode, metallic zinc is deposited at the cathode, and sulfuric acid is regenerated within the electrolyte.

Electrolytic zinc smelters contain a large number of cells-often several hundred. A portion of the electrical energy released in these cells dissipates as heat. The electrolyte is continuously circulated through cooling towers, both to lower its temperature and to concentrate the electrolyte through the evaporation of water. Routinely, half of the cathodes in a cell are disengaged for removal of zinc from the plates. The other half carry a higher current load. Occasionally, a complete cell shutdown occurs, such as when a cell is bypassed (using a Buss Bar to reroute current) for cleaning or repairing.

The final stage of electrolytic zinc smelting is the making and casting of the cathode zinc into small slabs (59 lb [27 kg]) or large slabs (1,408 to 2,420 lb [640 to 1,100 kg]).

A general diagram of the pyrometallurgical process is presented in Figure 4-12. Pyrometallurgical processing involves three major steps: roasting, sintering, and retorting.

Sintering is the first stage of the pyrometallurgical reduction of zinc oxide to slab zinc. Sintering removes lead and cadmium impurities by volatilization and produces an agglomerated permeable mass suitable for feed to retorting furnaces. Down-draft sintering machines of the Dwight-Lloyd type are used in the industry. Grate pallets are joined together for a continuous conveyor system. Combustion air is drawn down through the grate pallets and is exhausted to a particulate control system. The feed is a mixture of calcine, recycled sinter, and coke breeze, which is low-sulfur fuel. Having a low boiling point, oxides of lead and cadmium are volatilized from the sinter bed and are recovered in the particulate control system.

In retorting, because of the low boiling point of metallic zinc (1,663°F [906°C]), reduction and purification of zinc-bearing minerals can be accomplished to a greater extent than with most minerals. The sintered zinc oxide feed is brought into a high-temperature reducing atmosphere of 1,652 to 2,730°F (900 to 1,499°C). Under these conditions, the zinc oxide is simultaneously reduced and volatilized to gaseous zinc:

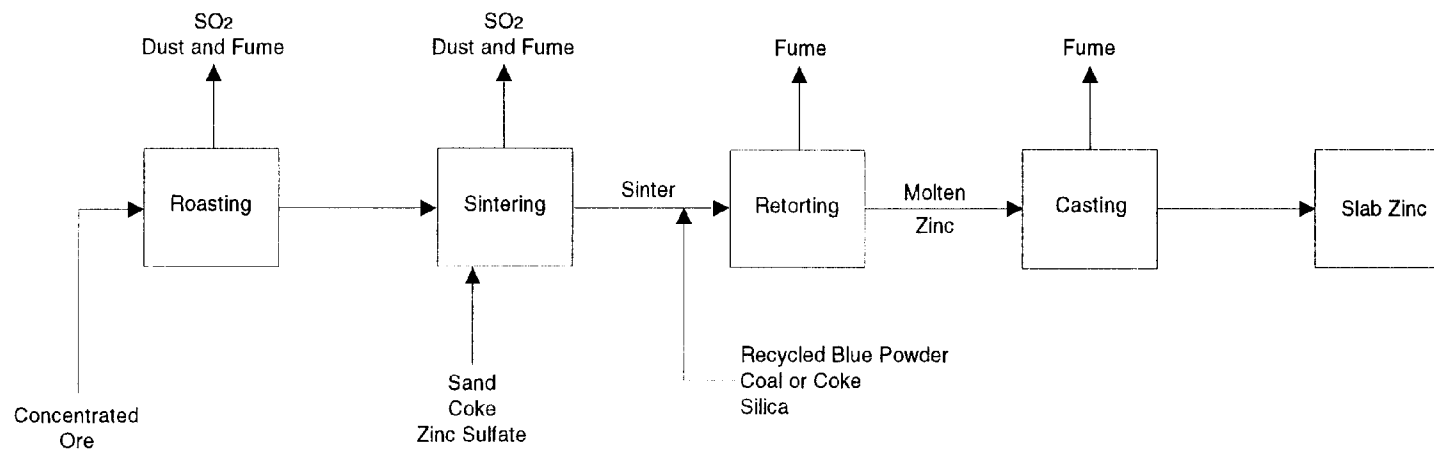


Figure 4-12. Pyrometallurgical Primary Zinc-Smelting Process

Source: Reference 35.





Carbon monoxide regeneration also occurs:



The zinc vapor and carbon monoxide that are produced pass from the main furnace to a condenser, where zinc recovery is accomplished by bubbling the gas mixture through a molten zinc bath. Retorting furnaces can be heated either externally by combustion flames or internally by electric resistance heating. The latter approach, electrothermic reduction, is the only method currently practiced in the United States, and it has greater thermal efficiency than do external heating methods. In a retort furnace, preheated coke and sinter, silica, and miscellaneous zinc-bearing materials are fed continuously in the top of the furnace. Feed coke serves as the principal electrical conductor, producing heat; it also provides the carbon monoxide required for zinc oxide reduction. Further purification steps can be performed on the molten metal collected in the condenser. The molten zinc finally is cast into small slabs (59 lb [27 kg]) or large slabs (1,408 to 2,420 lb [640 to 1,100 kg]).<sup>35</sup>

#### 4.5.3 Emissions

All four smelters treat the SO<sub>2</sub>-rich roaster exhaust gases in a sulfuric acid plant for SO<sub>2</sub> removal. As a result, particulate and lead emissions are negligible. The balance of the processes performed at the electrolytic plants are wet and do not produce emissions. Uncontrolled emissions from electrothermic reduction furnaces are also negligible. Thus, the only potentially significant source of particulate and lead emissions from primary zinc smelting operations in the United States is the one sinter machine operated at the pyrometallurgical plant. The sinter machine at this plant is currently controlled by three ESPs and one baghouse in series.<sup>18</sup> Lead emission factors for primary zinc production are not available.

## 4.6 SECONDARY ALUMINUM OPERATIONS

### 4.6.1 Source Description

Secondary aluminum operations involve the cleaning, melting, refining, alloying, and pouring of aluminum recovered from scrap, foundry returns, and dross. The processes used to convert scrap aluminum to secondary aluminum products such as lightweight metal alloy for industrial castings and ingots are presented in Figures 4-13 and 4-14. Production involves two general classes of operations: scrap treatment and smelting/refining. Except where otherwise indicated, this section is derived from Section 12.8 of AP-42.<sup>38</sup>

### 4.6.2 Process Description

Scrap treatment involves receiving, sorting, and processing scrap to remove contaminants and prepare the material for smelting. Processes based on mechanical, pyrometallurgical, and hydrometallurgical techniques are used, and those employed are selected to suit the type of scrap processed.

The smelting/refining operation generally involves the following steps:

- |             |              |
|-------------|--------------|
| a. charging | f. demagging |
| b. melting  | g. degassing |
| c. fluxing  | h. skimming  |
| d. alloying | i. pouring   |
| e. mixing   |              |

All of these steps may occur at each facility, with process distinctions being the furnace type used and emissions characteristics. However, as with scrap treatment, not all of these steps are incorporated into the operations at a particular plant. Some steps may be combined or reordered, depending on furnace design, scrap quality, process inputs, and product specifications.

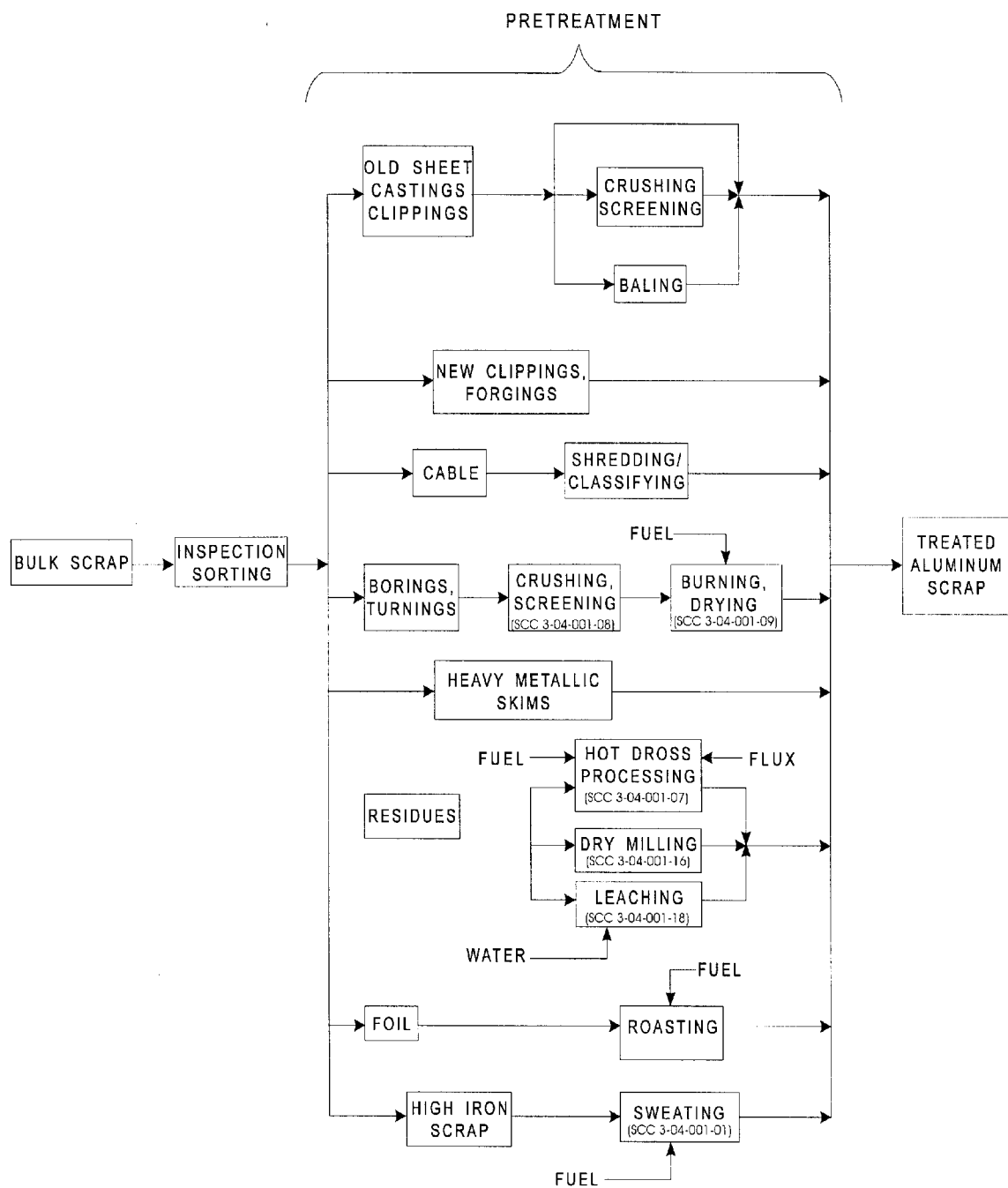


Figure 4-13. Typical Process Diagram for Pretreatment in the Secondary Aluminum Processing Industry

Source: Reference 38.

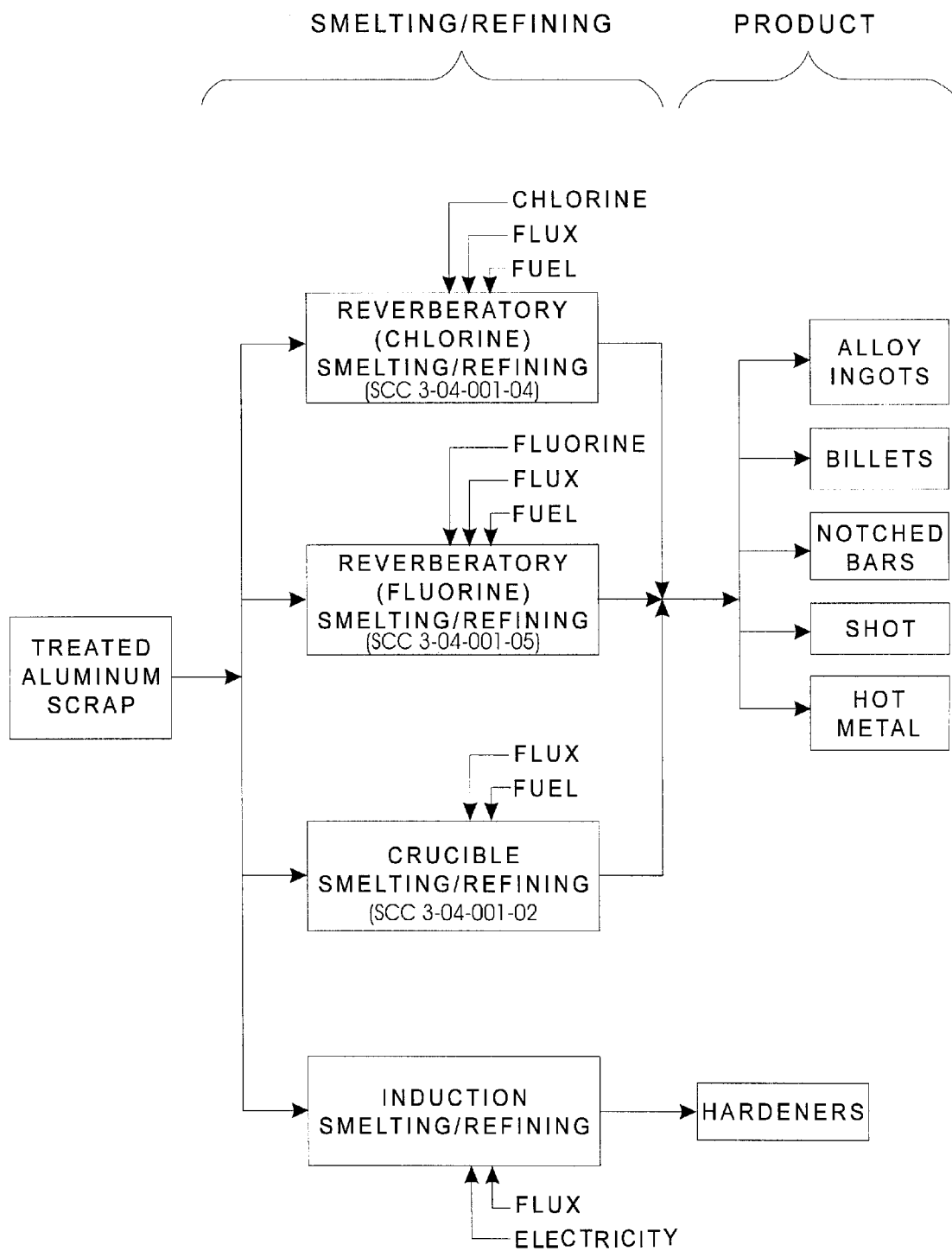


Figure 4-14. Typical Process Flow Diagram for the Secondary Aluminum Processing Industry

Source: Reference 38.

Purchased aluminum scrap undergoes inspection upon delivery and is sorted into the categories shown in Figure 4-13. Clean scrap requiring no treatment is transported to storage or is charged directly into the smelting furnace. The bulk of the scrap, however, must be manually sorted as it passes along a steel belt conveyor. Free iron, stainless steel, zinc, brass, and oversize materials are removed. The sorted scrap then goes to appropriate scrap treating processes, if necessary, or is charged directly to the smelting furnace. The more common scrap treatment processes are discussed in the following paragraphs.

Sorted scrap is conveyed to a ring crusher or hammer mill where the material is shredded and crushed, and the iron is torn away from the aluminum. The crushed material passes over vibrating screens to remove dirt and fines, and tramp iron is removed by magnetic drums and/or belt separators. Baling equipment compacts bulky aluminum scrap into bales.

Pure aluminum cable with steel reinforcement or plastic insulation is cut by alligator-type shears and granulated or further reduced in hammer mills to separate the iron core and the plastic coating from the aluminum. Magnetic processing removes the iron and air classification separates the insulation. Borings and turnings, in most cases, are treated to remove cutting oils, greases, moisture, and free iron. The processing steps involved are (1) crushing, (2) drying to remove oil and moisture, (3) screening to remove aluminum fines, (4) removing iron magnetically, and (5) storing the clean dried borings in tote boxes.

Several types of residue from primary and secondary aluminum plants contain recoverable amounts of aluminum. Aluminum is recovered from hot and cold drosses by batch fluxing in rotary furnaces. In the dry milling process, cold aluminum dross and other residues are processed by milling, screening, and concentrating to reduce oxides and non-metallic materials to fine powders, yielding a product which is 60 to 70 percent aluminum.

Drosses, skimmings, and slags are treated by leaching to remove fluxing salts and other nonrecoverable materials. First, the raw material is fed into a long, rotating drum or an attrition or ball mill, from which soluble contaminants are leached. The washed material is then screened to remove fines and dissolved salts and is dried and passed through a magnetic

separator to remove ferrous materials. The non-magnetic materials are then stored or charged directly to the smelting furnace.

Aluminum foil is treated by roasting to separate carbonaceous materials associated with the aluminum.

Sweating is a pyrometallurgical process using open-flame reverberatory furnaces to recover aluminum from scrap with high iron content. The aluminum and other constituents with low-melting temperatures melt, trickle down the hearth, through a grate, and into molds or collecting pots. The materials with higher-melting temperatures, including iron, brass, and oxidation products formed during the sweating process, remain in the furnace until they are removed. Treated aluminum scrap is transferred to the smelting/refining operations for refinement into finished products.

In smelting/refining operations, reverberatory furnaces are commonly used to convert clean, sorted scrap, sweated pigs, or untreated scrap to ingots, shot, or hot metal. The scrap is first mechanically charged to the furnace, often through charging wells designed to introduce chips and light scrap below the surface of a previously melted charge ("heel"). Batch processing is generally practiced for alloy ingot production, and continuous feeding and pouring are generally used for products having less strict specifications.

Cover fluxes are used to prevent oxidation of the melt caused by air contact. Solvent fluxes react with non-metallic materials, such as burned coating residues and dirt, to form insoluble materials that float to the surface as part of the slag. Alloying agents are charged to the furnace in amounts determined by product specifications. Nitrogen or other inert gases can be injected into the molten metal to help raise dissolved gases (typically hydrogen) and intermixed solids to the surface.

Demagging reduces the magnesium content of the molten charge from approximately 0.3 to 0.5 percent (typical scrap value) to about 0.1 percent (typical product line alloy specification). When demagging with chlorine gas, chlorine is injected under pressure

through carbon lances to react with magnesium and aluminum as it bubbles to the surface. Other chlorinating agents or fluxes, such as anhydrous aluminum chloride or chlorinated organic compounds, are sometimes used.

In the skimming step, contaminated semi-solid fluxes (dross, slag, or skimmings) are ladled from the surface of the melt and removed through the forewell. The melt is then cooled before pouring.

The reverberatory (fluorine) process is similar to the reverberatory (chlorine) smelting/refining process, except that aluminum fluoride ( $\text{AlF}_3$ ) is employed in the demagging step instead of chlorine. The  $\text{AlF}_3$  reacts with magnesium to produce molten metallic aluminum and solid magnesium fluoride salt, which floats to the surface of the molten aluminum and is skimmed off.

The crucible smelting/refining process is designed to produce harder aluminum alloys by blending pure aluminum and hardening agents in an electric induction furnace. The process steps include charging scrap to the furnace, melting, adding and blending the hardening agent, skimming, pouring, and casting into notched bars.

#### 4.6.3 Emissions and Emission Control Techniques

Each processing step in the secondary aluminum industry is a potential source of lead emissions, which are generally emitted as PM. Lead emissions will be a small fraction of total particulate emissions and will vary with the lead content of the scrap. Table 4-10 presents lead emission factors for specific processing units.

Data for lead emissions from secondary aluminum processing facilities was extremely limited. Currently, emissions data from secondary aluminum facilities are being

TABLE 4-10. LEAD EMISSION FACTORS FOR SECONDARY ALUMINUM PRODUCTION

SCC Number	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
3-04-001-09	Burning/Drying	Venturi Scrubber	4.36x10 <sup>-3</sup> (2.18x10 <sup>-3</sup> )	2.02x10 <sup>-3</sup> - 7.04x10 <sup>-3</sup> (1.01x10 <sup>-3</sup> - 3.52x10 <sup>-3</sup> )	U	39
		Baghouse	1.04x10 <sup>-5</sup> (5.18x10 <sup>-6</sup> )	6.76x10 <sup>-6</sup> - 1.48x10 <sup>-5</sup> (3.38x10 <sup>-6</sup> - 7.40x10 <sup>-6</sup> )	U	39
		Multiple Cyclones	2.16x10 <sup>-2</sup> (1.08x10 <sup>-2</sup> )	2.10x10 <sup>-2</sup> - 2.26x10 <sup>-2</sup> (1.05x10 <sup>-2</sup> - 1.13x10 <sup>-2</sup> )	U	40
3-04-001-14	Reverberatory Furnace	Baghouse	1.4x10 <sup>-3</sup> (7.0x10 <sup>-4</sup> ) <sup>b</sup>	1.0x10 <sup>-3</sup> - 2.2x10 <sup>-3</sup> (5.0x10 <sup>-4</sup> - 1.1x10 <sup>-3</sup> ) <sup>b</sup>	D	41

<sup>a</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of aluminum produced, except as noted.

<sup>b</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of aluminum processed.



collected for inclusion in the secondary aluminum MACT, which may augment the information provided here.

There is potential for particulate emissions from several processing steps, including crushing/screening, shredding/classifying, bailing, burning/drying, dross processing, roasting, smelting/refining, and demagging. Particulate emissions may also be released by leaching operations during drying. Fumes may be emitted from fluxing reactions. Lead emission levels from each of these processes depend on the lead content of the feed introduced to each unit step.

Typical control devices at secondary aluminum operations include baghouses, multicyclones, scrubbers, and local ventilation. Although, these have been designed primarily for PM control, in controlling PM, lead emissions are controlled.

#### 4.7 IRON AND STEEL FOUNDRIES

##### 4.7.1 Source Location

There were approximately 756 iron and steel foundries in the United States in 1992 based on a survey conducted by the EPA to support development of the iron and steel foundry Maximum Achievable Control Technology (MACT) standard.<sup>42</sup> In general, foundries are located in areas of heavy industry and manufacturing, especially areas where iron and steel are produced (e.g., the Great Lakes States).

##### 4.7.2 Process Description

Iron and steel foundries can be defined as those that produce gray, white, ductile, or malleable iron and steel castings. Both cast irons and steels are solid solutions of iron, carbon, and various alloying materials. Although there are many types of iron and steel, groups can be distinguished by their carbon content. Cast iron typically contains 2 percent carbon or greater; cast steel usually contains less than 2 percent carbon.<sup>40</sup>

Iron castings are used in most types of mechanical equipment, including motor vehicles, farm machinery, construction machinery, petroleum industry equipment, electrical motors, and iron and steel industry equipment.

Steel castings are used in motor vehicles, railroad equipment, construction machinery, aircraft, agricultural equipment, ore refining machinery, and chemical manufacturing equipment.<sup>43</sup> Steel castings are classified on the basis of their composition and heat treatment, which determine their end use. Classifications include carbon, low-alloy, general-purpose-structural, heat-resistant, corrosion-resistant, and wear-resistant.

The following four basic operations are performed in all iron and steel foundries:

- Storage and handling of raw materials;
- Melting of scrap or ingot metal;
- Transfer of the hot molten metal into molds; and
- Preparation of the molds to hold the molten metal.

Other processes present in most, but not all, foundries include:

- Sand preparation and handling;
- Mold cooling and shakeout;
- Casting cleaning, heat treating, and finishing;
- Coremaking; and
- Pattern making.

A generic process flow diagram for iron and steel foundries is shown in Figure 4-15. Figure 4-16 identifies the emission points in a typical iron and steel foundry.

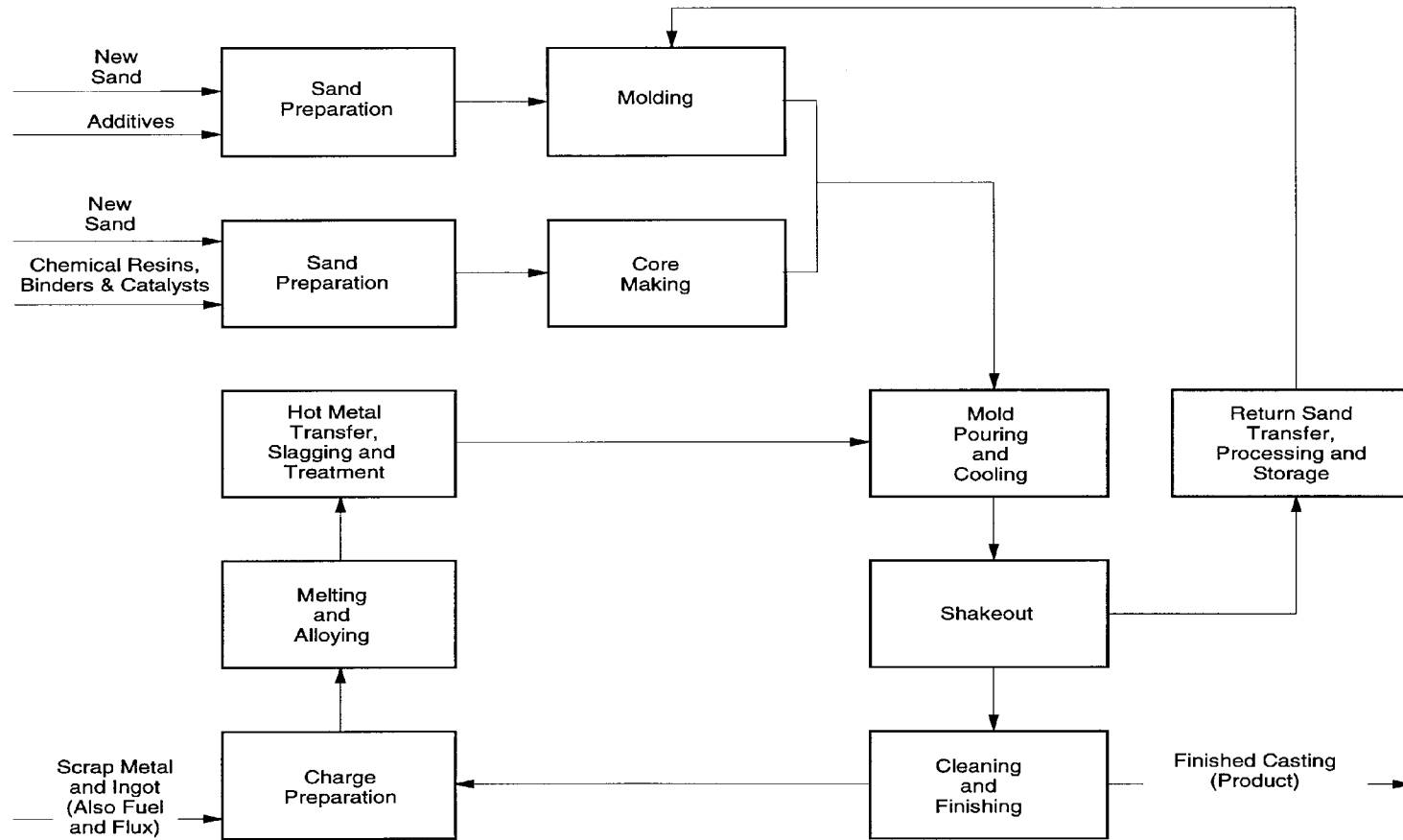


Figure 4-15. Process Flow Diagram for a Typical Sand-Cast Iron and Steel Foundry

Source: Reference 43.

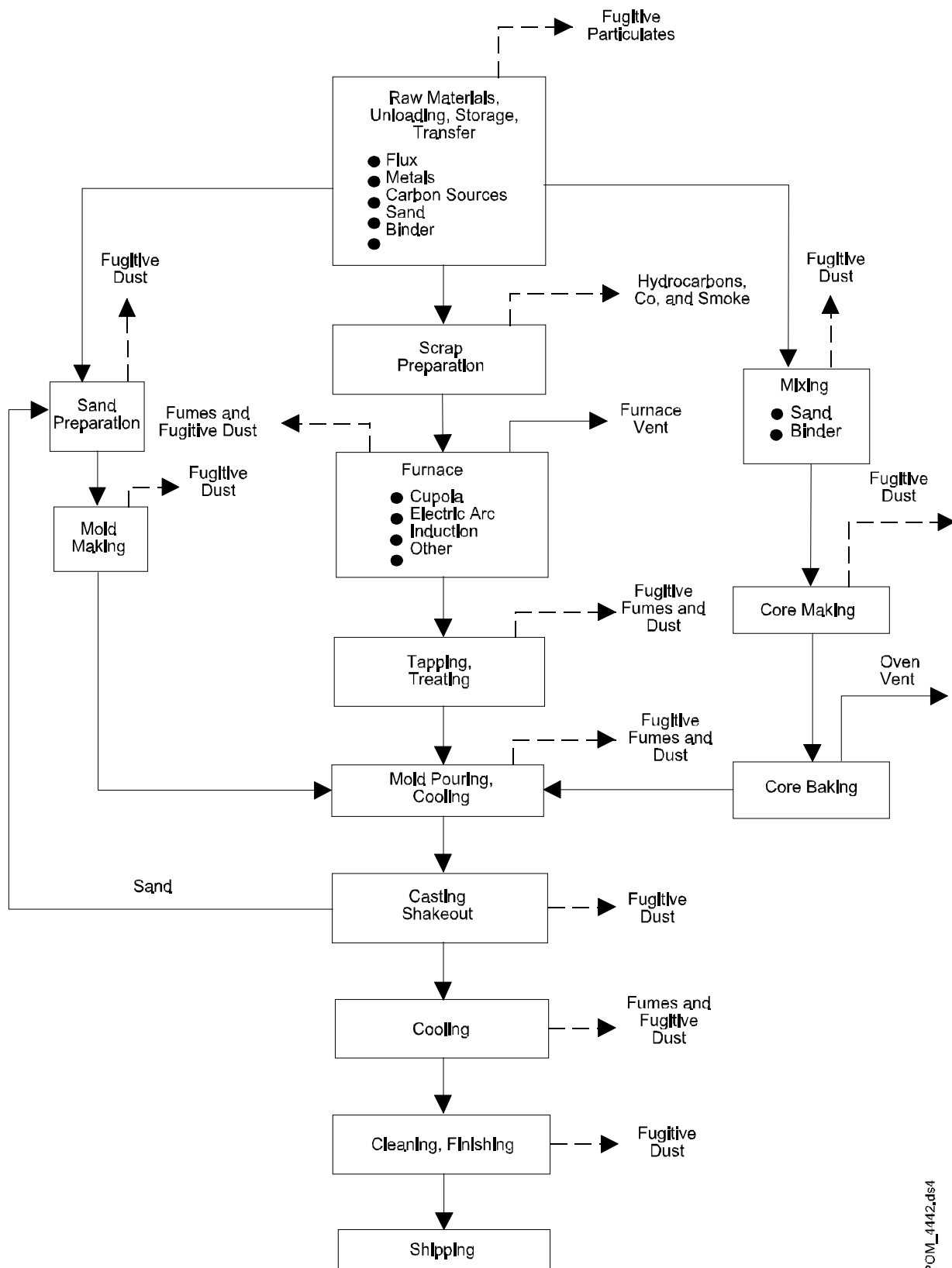


Figure 4-16. Emission Points in a Typical Iron and Steel Foundry

Source: Reference 44

## Metal Melting Process

The highest amount of metal (by volume) in iron and steel foundries is melted in cupolas. Electric arc furnaces (EAFs) and induction furnaces are also commonly used. Cupolas are charged with alternate layers of coke, metallics, and fluxes. Combustion air is introduced into the cupola through tuyeres located at the base. The heat produced by the burning coke melts the iron, which flows down and is tapped from the bottom of the cupola. Fluxes combine with non-metallic impurities in the charge and form slag, which is removed through tap holes located above the level of the metal tap hole. Cupola capacities range mostly from 1 to 30 tons (1 to 27 Mg) per hour, with a few large units capable of producing close to 100 tons (90 Mg) per hour. Larger furnaces are operated for several days at a time with inspections and cleanings between melt cycles.<sup>45</sup>

Iron and steel castings are produced in a foundry by injecting or pouring molten metal into cavities of a mold made of sand, metal, or ceramic material. The use of EAFs and induction furnaces is increasing. Steel foundries rely almost exclusively on EAFs or induction furnaces for melting purposes.

In all types of foundries, when the poured metal has solidified, the molds are separated and the castings removed from the mold flasks on a casting shakeout unit. Cutoff, abrasive (shotblasting) cleaning, grinding, and heat treating are performed as necessary. The castings are then inspected and shipped to plants of other industries for machining and/or assembly into final products.<sup>43</sup>

In a typical foundry operation, charges to the melting unit are sorted by size and density and cleaned (as required) prior to being put into the melter. Charges consist of scrap metal, ingot, carbon (coke), and flux. Prepared charge materials are placed in crane buckets, weighed, and transferred into the melting furnace or cupola. The charge in a furnace or cupola is heated until it reaches a certain temperature and the desired product chemistry of the melt has been attained. After the desired product is obtained, the molten metal is poured out of the furnace into various-size transfer ladles and then into the molds holding furnaces.

## Mold and Core Production

The casting or mold pouring and cooling operations in iron and steel foundries are suspected to be a source of lead emissions. In addition to casting, mold preparation and casting shakeout (removal from the mold) activities are also suspected as lead emission sources. Lead emissions from these processes are believed to be small, although test data are not available to quantify actual lead emissions.

### 4.7.3 Emission Control Techniques

Lead emissions depend mostly on the scrap metal quality and control technologies. Control technologies commonly used to control lead emissions from iron and steel foundry metal melting operations include baghouses and wet scrubbers. Additionally, lead emissions due to coke combustion may be reduced by substituting natural gas for coke as a heat source. Potential lead emissions from molding, casting, and shakeout are fugitive in nature. Fugitive emissions from such sources are generally controlled with local hooding or building ventilation systems that are ducted to a control device (predominantly baghouses).<sup>45</sup>

### 4.7.4 Emissions

Lead emission factors for several iron foundry processes were available. These emission factors are presented in Table 4-11.

## 4.8 ORE MINING, CRUSHING, AND GRINDING

### 4.8.1 Source Description

Lead emissions are generated by the mining, crushing, and grinding of three primary nonferrous metal ores: lead, zinc, and copper. Lead and zinc ores are normally mined underground, whereas copper ores are normally mined in open pits.<sup>46</sup> Lead, zinc, and copper occur in various amounts in all three ore types. If the metal content of two or more metals is high

TABLE 4-11. LEAD EMISSION FACTORS FOR IRON AND STEEL FOUNDRIES

SCC Number	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating	Reference
3-04-003-01	Iron Foundry - Cupola	None	---	1.00x10 <sup>-1</sup> - 1.10 (5.00x10 <sup>-2</sup> - 1.10)	B	47
		Afterburner/ Venturi Scrubber	1.56x10 <sup>-3</sup> (7.80x10 <sup>-4</sup> ) <sup>b</sup>	---	U	3
		Baghouse	2.67x10 <sup>-3</sup> (1.34x10 <sup>-3</sup> )	1.39x10 <sup>-3</sup> - 4.45x10 <sup>-3</sup> (6.95x10 <sup>-4</sup> - 2.23x10 <sup>-3</sup> )	U	48
3-04-003-02	Iron Foundry - Reverberatory Furnace	None	---	1.20x10 <sup>-2</sup> - 1.40x10 <sup>-1</sup> (6.00x10 <sup>-3</sup> - 7.00x10 <sup>-2</sup> )	B	47
3-04-003-03	Iron Foundry - Electric Induction Furnace	None	---	9.00x10 <sup>-3</sup> - 1.00x10 <sup>-1</sup> (4.45x10 <sup>-3</sup> - 5.00x10 <sup>-2</sup> )	B	47
3-04-003-20	Iron Foundry - Casting	Afterburner/ Venturi Scrubber	4.80x10 <sup>-3</sup> (2.40x10 <sup>-3</sup> ) <sup>b</sup>	---	U	3

<sup>a</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of iron/steel produced, except as noted.

<sup>b</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of material processed.

"---" means data not available.

enough for economical extraction, the ore is listed as a mixed ore (e.g., lead-zinc, copper-lead). Except where otherwise indicated, this section is derived from *Control Techniques for Lead Air Emissions*.<sup>18</sup>

#### 4.8.2 Process Description

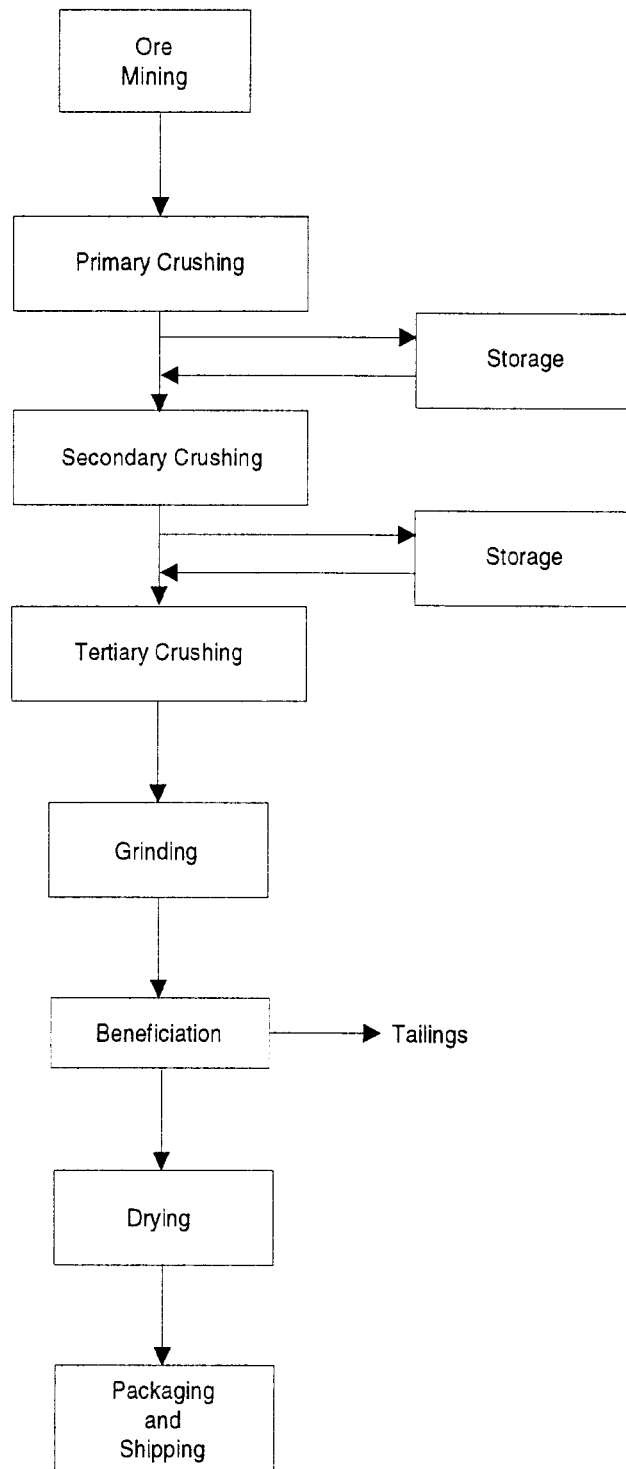
Lead, zinc, and copper ores are generally concentrated in a liquid medium using settling and flotation. In all but a few cases, the metal is combined with sulfur and/or oxygen in the ore. Lead, zinc, and copper are usually found together in varying percentages in ore deposits.<sup>46</sup> Depending on the amount of each of these metals in the ore and on the potential economic return, the metals are either separated from the ore or discarded in the tailings.

The ore in the underground mines is disintegrated by light-weight percussive and rotary-percussive drilling machines. Power shovels, front-end loaders, scrapers, and mucking machines load the pulverized ore into electric or diesel-powered motorized trains operating on heavy-gauge tracks, or into trackless shuttle cars. The ore is commonly run through a primary crusher underground and then conveyed by skip loader, rail tram, or conveyor belt (depending on the mine depth) to the surface, where classifying and additional grinding occur. Figure 4-17 illustrates a typical ore crushing and grinding operation.

Lead and zinc ores are concentrated to 45 to 75 percent before going to the smelter. Depending on the mineral and gauge material, the ore is crushed and ground to a size based on an economic balance between the recoverable metal values and the cost of grinding. Standard jaw, gyratory, and cone crushers, vibrating or trommel screens, and rod and ball mills are used to reduce the ore to powder in the 65- to 325-mesh range. Through gravity and/or selective flotation, the finely divided particles of copper, lead, and zinc are separated from the gangue and are cleaned, thickened, filtered, and dried.

Copper ores are handled in essentially the same manner as zinc and lead ores. Open-pit mining for copper, copper-lead, copper-zinc, and copper-lead-zinc ores is centered





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Figure 4-17. Process Diagram for Ore Mining and Crushing

Source: Reference 46.

primarily in the Western U.S. in arid or semi-arid areas. The ore and gangue are loosened and pulverized by explosives, scooped up by power shovels or other mechanical equipment, and loaded into trucks, rail trains, or cars for transport to the concentrator. The ore is then processed in the same manner as lead and zinc ores.

#### 4.8.3        Emissions

Lead emissions are basically fugitive in nature and are caused by drilling, blasting, loading, conveying, screening, unloading, crushing, and grinding operations.<sup>46</sup> The emissions from actual ore mining operations are contained in underground mines. Lead emission factors from available literature sources are presented in Table 4-12. Lead emissions from lead, copper, or zinc ore mining are dependent upon the lead content of the ore. Ores with greater lead content produce greater lead emission factors. Mixed-ore mining produces relatively constant emission rates, although the lead content of the ore varies.

#### 4.8.4        Emission Control Techniques

Because of the diversity of particulate emission sources in ore mining and operations, a variety of control methods and techniques have been used. Dust-suppression techniques are the most commonly used. They are designed to prevent PM from becoming airborne and are applicable to both process and fugitive dust sources. Particulate emissions such as those generated by crushing operations can be captured using local hooding and ventilation and collected in control devices. Emission sources and applicable control options are listed in Table 4-13.

### 4.9            BRASS AND BRONZE PROCESSING

#### 4.9.1        Source Description

Brass and bronze are generally considered to be copper-based alloys, with zinc, tin, and other metals such as lead, aluminum, manganese, and silicon as secondary components.

TABLE 4-12. LEAD EMISSION FACTORS FOR LEADBEARING ORE CRUSHING AND GRINDING

SCC Number	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Range in lb/ton (kg/Mg) <sup>a</sup>	Emission Factor Rating
3-03-031-01	Lead Ore (5.1% Pb content)	None	3.00x10 <sup>-1</sup> (1.50x10 <sup>-1</sup> )	---	B
3-03-031-02	Zinc Ore (0.2% Pb content)	None	1.20x10 <sup>-2</sup> (6.00x10 <sup>-3</sup> )	---	B
3-03-031-03	Copper Ore (0.2% Pb content)	None	1.20x10 <sup>-2</sup> (6.00x10 <sup>-3</sup> )	---	B
3-03-031-04	Lead-Zinc Ore (2.0% Pb content)	None	1.20x10 <sup>-1</sup> (6.00x10 <sup>-2</sup> )	---	B
3-03-031-05	Copper-Lead Ore (2.0% Pb content)	None	1.20x10 <sup>-1</sup> (6.00x10 <sup>-2</sup> )	---	B
3-03-031-06	Copper-Zinc Ore (0.2% Pb content)	None	1.20x10 <sup>-2</sup> (6.00x10 <sup>-3</sup> )	---	B
3-03-031-07	Copper-Lead-Zinc Ore (2.0% Pb content)	None	1.20x10 <sup>-1</sup> (6.00x10 <sup>-2</sup> )	---	B

Source: Reference 49

<sup>a</sup> Emission factors are expressed in lb (kg) of pollutant emitted per ton (Mg) of ore processed.

"---" means data not available.

TABLE 4-13. EMISSION SOURCES AND CONTROL DEVICES

Operation or Source	Control Options
Drilling	Liquid injection (water or water plus a wetting agent) Capturing and venting emissions to a control device
Blasting	No control Good blasting practices
Loading	Water wetting
Hauling (emissions from roads)	Water wetting Treatment with surface agents Soil stabilization Paving Traffic control
Crushing	Wet-dust suppression systems Capturing and venting emissions to a control device
Screening	Same as for crushing
Conveying (transfer points)	Same as for crushing
Stockpiling	Stone ladders Stacker conveyors Water sprays at conveyor discharge
Conveying	Covering Wet-dust suppression
Windblown dust from stockpiles	Water wetting Surface active agents Covering Windbreaks
Windblown dust on roads	Oiling Surface active agents Soil stabilization Paving Sweeping

Source: Reference 18

In 1987, the production of brass and bronze ingots totalled 203,934 tons (185,058 Mg).<sup>18</sup> Of this total, about 19 percent consisted of tin bronze, aluminum bronze, and nickel bronze, which do not contain appreciable amounts of lead. The remaining 81 percent consisted of leaded red and semi-red brass, high-leaded tin bronze, yellow brass, and manganese bronze, all of which contain significant amounts of lead. Except where otherwise indicated, this section is derived from *Control Technologies for Lead Air Emissions*.<sup>18</sup>

#### 4.9.2 Process Description

Figure 4-18 illustrates the processes involved in the production of brass and bronze alloys. The principal processes include scrap metal pretreatment and smelting. Feed materials consist primarily of high-grade copper and copper alloy (brass and bronze) scrap.

Scrap pretreatment can be accomplished using several different techniques in combination or separately, depending on the type and grade of scrap to be treated. Mechanical, pyrometallurgical, and hydro-metallurgical processes may be used. Generally, the feed scrap is first concentrated by manual and mechanical means, including manual sorting, stripping, shredding, magnetic separation, and briquetting. Pyrometallurgical processes may include sweating to remove low-melting metals such as lead, solder, and babbitt; burning to remove insulation from wire or cable scrap; and drying to eliminate volatile oils and cutting fluids from machine shop scrap. Hydro-metallurgical processes include floatation and leaching.<sup>34</sup>

Melting, smelting, and alloying are performed in a variety of furnace types, including stationary and rotary reverberatory furnaces, electric furnaces, and crucible or pot furnaces. First, the pretreated and clean scrap, along with fluxes, are charged to the melting furnace. The charge materials are then melted by direct or indirect heat supplied by gas or oil combustion in fossil fuel-fired furnaces, and by electric arc resistance or induction in the electric furnaces. Metal oxides and other impurities in the melt react with fluxes to form a slag, which is skimmed off and generally discarded. Alloying metals are added as required to bring the mixture to the desired final composition. In addition, air and oxygen may be blown into the smelt to

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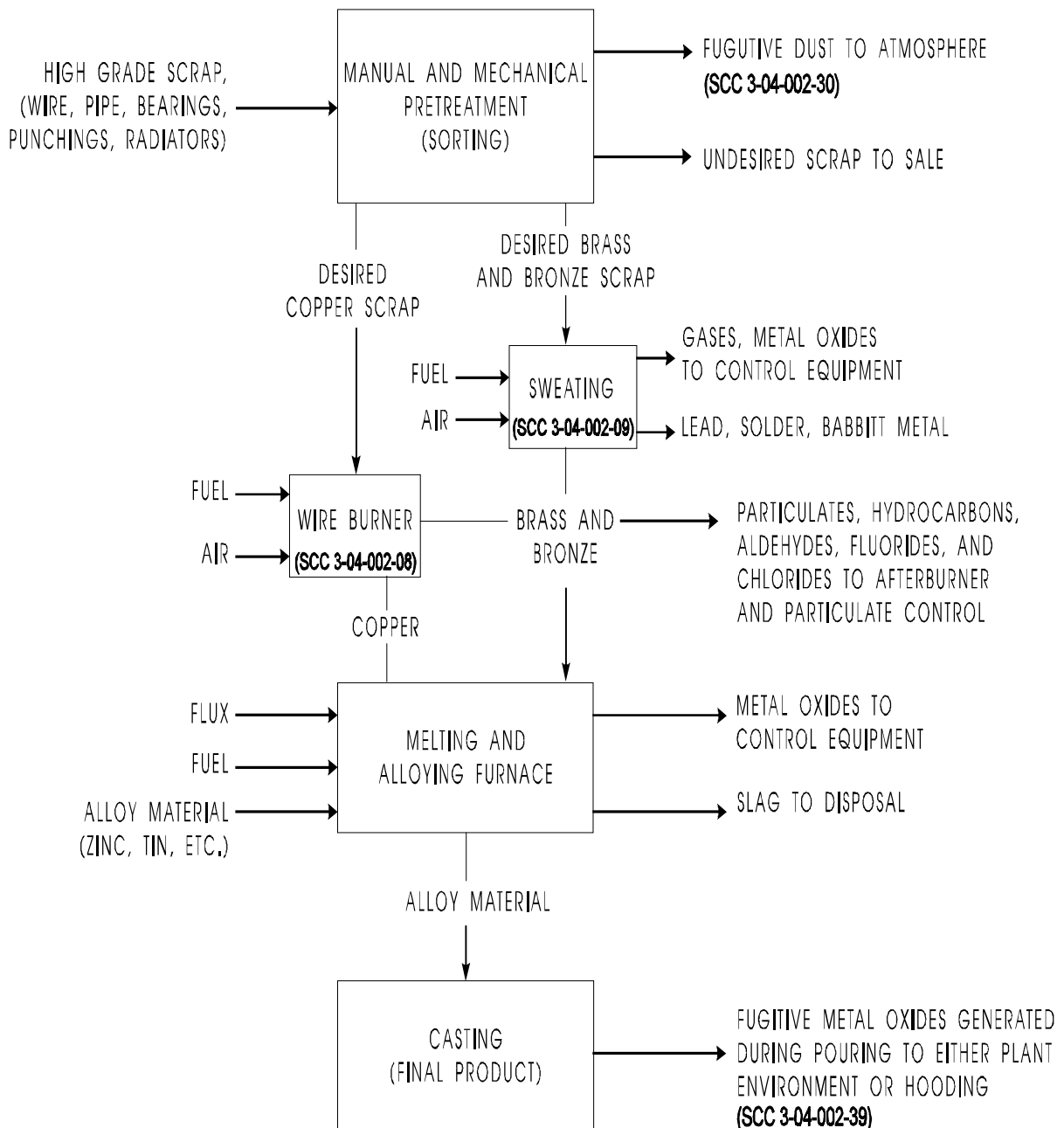


Figure 4-18. Brass and Bronze Alloys Production Processes

Source: Reference 34.

oxidize excess zinc. After the desired final composition is reached, the refined metal product is poured or tapped into ingots or other cast shapes.<sup>34</sup>

#### 4.9.3 Emissions

Scrap treatment by mechanical and hydrometallurgical processes at brass and bronze manufacturing facilities produces little or no emissions. Pyrometallurgical treatment processes may generate substantial emissions, including combustion products and contaminants, but few metal oxides such as lead oxide. Wire burning generates much PM, consisting largely of unburned combustibles. Lead may be emitted as PM from wire burning depending on the lead content of the charge. Scrap drying and cutting produces large amounts of soot and hydrocarbons but little or no metal oxides such as lead oxide. Sweating operations may produce small amounts of metal oxides, which are typically controlled by baghouses.

Air pollutants emitted from brass and bronze smelting furnaces consist of products of combustion, dusts, and metallic fumes resulting from the oxidation and condensation of the more volatile metals such as lead, zinc, and others. The lead fraction of the PM generated will vary according to fuel type, alloy composition, furnace type, smelting temperature, and other operational factors. Exhaust gas parameters for an uncontrolled brass and bronze reverberatory furnace are presented in Table 4-14. Table 4-15 shows production data and emission factors.

TABLE 4-14. CHARACTERISTICS OF UNCONTROLLED EXHAUST GAS FROM  
A BRASS AND BRONZE REVERBERATORY FURNACE

Parameters	Standard International Units	English Units
Gas flow rate <sup>a</sup>	4.5 m <sup>3</sup> /s*Mg*h <sup>-1</sup> product	8600 acfm/tph product
Temperature <sup>b</sup>	925 - 1315 C	1700 - 2400 °F
Grain loading	0.12 - 9.4 g/m <sup>3</sup>	0.05 - 4.1 gr/scf
Particle size distribution	0.03 - 0.5 mm (majority)	
Lead content of particulate	high-leaded 58% wt yellow and red 15% wt other brass and bronze 7% wt	

Source: Reference 18

<sup>a</sup> Flow rates can vary according to the hooding arrangement. Volume given is at 250°F (120°C).

<sup>b</sup> Temperature is usually reduced to 250°F (120°C).

TABLE 4-15. BRASS AND BRONZE PRODUCTION AND LEAD EMISSIONS IN 1992

Product	Production <sup>a</sup> tons (Mg)	Pb Emission Factor <sup>b</sup> lb/ton (kg/Mg)
High-leaded alloys <sup>c</sup>	21,285 (19,309)	50 (25)
Red and Yellow lead alloys <sup>d</sup>	119,986 (108,880)	13.2 (6.6)
Other alloys <sup>e</sup>	21,803 (19,785)	5.0 (2.5)
Total	163,073 (147,974)	

<sup>a</sup> The U.S. Bureau of Mines provided total lead alloy production for 1992. The breakdown of production for each alloy type was not available. Therefore, the 1992 production estimates for each alloy type are based on the breakdown of total lead production for each alloy type in 1986. Total lead alloy production was estimated to be 163,073 tons (147,974 Mg). Source: Reference 18, 53

<sup>b</sup> Source: Reference 18

<sup>c</sup> Includes all production of high-leaded tin bronze; 90 percent of production for manganese bronze; and silicon brass and bronze.

<sup>d</sup> Includes all production of leaded red brass, semi-red brass, and yellow brass.

<sup>e</sup> Includes all production for copper-base hardness and master alloys, miscellaneous alloys, 10 percent of manganese bronze, and silicon brass and bronze.